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IN ENGLISH TRANSLATION

CONSULTANTS BUREAU, INC.

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Mikhail Mikhailovich Shemiakin

Deeply respected Mikhail Mikhailovich:

The Division of Chemical Science of the Academy of Sciences USSR and the Editorial Committee of the Bulletin of the Academy of Sciences USSR, Division of Chemical Science, heartily congratulates you on your fiftieth birthday.

Your studies in the field of the chemistry of natural and biologically active compounds, especially the widely developed work on the chemistry and the biochemistry of antibiotics, as well as work in theoretical organic chemistry and synthesis, are all well known to a wide circle of chemists. You have succeeded in combining successfully your scientific work with a considerable amount of scientific organizational work in the Division of Chemical Science.

We wish you, dear Mikhail Mikhailovich, good health and further creative successes.

Division of Chemical Science of
the Academy of Sciences USSR
and Editorial Committee of the
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Martin Izrailevich Kabachnik

Deeply respected Martin Izrailevich:

The Division of Chemical Science of the Academy of Sciences USSR and the Editorial Committee of the Bulletin of the Academy of Sciences USSR, Division of Chemical Science, heartily congratulate you on the fiftieth anniversary of your birth and on the thirtieth anniversary of your multilateral scientific activity.

Your studies in the field of chemistry of organophosphorus compounds and the theory of tautomeric equilibria are well known to a wide circle of organic chemists.

We wish you, dear Martin Izrailevich, health and further creative successes in your scientific activity.

Division of Chemical Science
of the Academy of Sciences USSR
and Editorial Committee of the
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A STUDY OF SYSTEMS CONTAINING CONCENTRATED HYDROGEN PEROXIDE

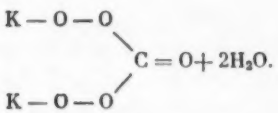
14. SOLUBILITY ISOTHERMS OF THE TERNARY SYSTEM $K_2CO_3-H_2O_2-H_2O$

S. Z. Makarov and V. N. Chamova

INTRODUCTION

It had been shown for the system $Na_2CO_3-H_2O_2-H_2O$, studied by us earlier [1], that only perhydrates – products of addition of hydrogen peroxide to sodium carbonate: $Na_2CO_3 \cdot H_2O \cdot 1.5\ H_2O_2$, $Na_2CO_3 \cdot H_2O \cdot 2H_2O_2$ and $Na_2CO_3 \cdot 2H_2O_2$ – are formed in the reaction of sodium carbonate with aqueous solutions of hydrogen peroxide in the temperature interval of 0-20°. "True peroxide compounds" – percarbonates – are not formed in this reaction, Tanatar's concepts to the contrary notwithstanding [2].

It was shown in Kazanetskii's work [3] that two compounds, which differ in the amount of active oxygen and which have the general composition: $K_2CO_3 \cdot 2H_2O_2 \cdot 0.5\ H_2O$ and $K_2CO_3 \cdot 3H_2O_2$, may be obtained by the treatment of potassium carbonate with 25% hydrogen peroxide solution. Kazanetskii concluded, on the basis of analytical data, that these compounds may be regarded as either molecular compounds of potassium carbonate and hydrogen peroxide, or as salts of carbonic acid in which both hydrogens of the aqueous residue are replaced by peroxidic groups, i.e., $K_2CO_3 \cdot 2H_2O_2 \cdot 0.5H_2O$, or



The synthetic method of the preparation and the volume of research done on the perhydrates of alkali metal carbonates are insufficient in themselves for a categoric affirmation of their structure. However, one may expect, by analogy with the previously studied solid phases in the system $Na_2CO_3-H_2O_2-H_2O$ [1], that potassium carbonate will form compounds of the perhydrate type, rather than hydrates of percarbonates, with aqueous hydrogen peroxide solutions.

At the same time it should be noted that the fundamental component of the $K_2CO_3-H_2O_2-H_2O$ system – potassium carbonate – has been studied sufficiently well in the past and that the data on its solubility can be found in all reference books. Two hydrates are known: $K_2CO_3 \cdot 1.5H_2O$ which is stable to −6.2° and a hydrate $K_2CO_3 \cdot 6H_2O$ which exists in equilibrium with saturated aqueous solutions from −6.2° to the eutectic temperature of −36.5°. No other hydrated forms of potassium carbonates are shown in the literature.

EXPERIMENTAL

The study of the $K_2CO_3-H_2O_2-H_2O$ system by the method of solubility was run at 20° in a thermostat provided with a toluene thermoregulator and at 0° and at −10° in a Dewar flask with ice or with a freezing mixture. Products of high purity: $K_2CO_3 \cdot 6H_2O$, $K_2CO_3 \cdot 1.5H_2O$ and $K_2CO_3 \cdot 3H_2O_2$, were used as the starting materials. We prepared chemically pure K_2CO_3, containing not less than 99.64% of potassium carbonate, by heating chemically pure $KHCO_3$ to 200-250°. The $K_2CO_3 \cdot 1.5H_2O$ was prepared by evaporation and crystallization of solutions of potassium carbonate in water, while $K_2CO_3 \cdot 6H_2O$ was prepared from potassium carbonate solution, saturated at room temperature, by chilling it to −5°. Initially we prepared $K_2CO_3 \cdot 3H_2O_2$ by the action of 25%

hydrogen peroxide on potassium carbonate in the ratio of one part by weight of K_2CO_3 to five parts by weight of 25% hydrogen peroxide. Upon addition of ethyl alcohol to this mixture, the latter formed two layers with the appearance of a layer of a heavy, oily liquid; rhombic crystals with the composition of $K_2CO_3 \cdot 3H_2O_2$ separated from this liquid after several hours in the cold at −15°. An analysis of these crystals, prepared according to a method given in the literature, gave: K_2CO_3 58.32%, H_2O_2 41.58%; the theoretical contents being: K_2CO_3 57.54% and H_2O_2 42.46%. One of the salts described above and the hydrogen peroxide solution of various concentrations were charged into the vessel for solubility determination. Equilibrium was established in the solutions of this system after 1-2 hours. The content of K_2CO_3 in test samples was determined by titration with 0.1N sulfuric acid in the presence of Methyl orange after the decomposition of hydrogen peroxide. The content of hydrogen peroxide or that of active oxygen was determined by titration with 0.1 N potassium permanganate solution in 1 : 5 sulfuric acid. The resulting analytical data were recalculated to K_2CO_3, H_2O_2 and H_2O and were then plotted on the triangular phase diagram. The solid phase composition was determined by the method of residues and was corrected microscopically.

1. The 0°C isotherm. We used $K_2CO_3 \cdot 6H_2O$, $K_2CO_3 \cdot 1.5H_2O$ and $K_2CO_3 \cdot 3H_2O_2$ as the possible solid phases, in the study of equilibria at 0°. Under these conditions, the crystals of $K_2CO_3 \cdot 6H_2O$ which were introduced immediately went into the previously unknown hydrate $K_2CO_3 \cdot 4H_2O$. At the same time the solutions turned out to contain a greatly lowered content of potassium carbonate (by more than a factor of 3) relative to solutions saturated with $K_2CO_3 \cdot 1.5H_2O$. The solubility of K_2CO_3 in water, in equilibrium with the solid phase of $K_2CO_3 \cdot 4H_2O$, was equal to 15.0% and increased steadily, with increasing content of H_2O_2 in the solution, reaching the maximum value of 38.24% at the transition point 17 of the above diagram (Fig. 1) with solid phase of $K_2CO_3 \cdot 4H_2O + K_2CO_3 \cdot 2H_2O_2$. At still higher levels (above 26.6%) of hydrogen peroxide in the solution, the equilibrium solid phase was the triperhydrate of potassium carbonate which was traced up to H_2O_2 concentrations of 48.8%. Thus, the 0° isotherm is characterized, under the conditions of stable equilibrium, by the presence of but two branches which correspond to the conditions of existence of two solid phases: $K_2CO_3 \cdot 4H_2O$ and $K_2CO_3 \cdot 3H_2O_2$ in equilibrium with the liquid phases. These results are rather interesting since according to the literature data $K_2CO_3 \cdot 3H_2O_2$ does not separate from solutions, existing evidently under conditions of strong supersaturation, and may be obtained only after prolonged freezing the solutions containing H_2O_2 and K_2CO_3. If one takes, as the initial solid phase, the usual hydrate $K_2CO_3 \cdot 1.5H_2O$, instead of $K_2CO_3 \cdot 6H_2O$, there occur some significant changes in the content of K_2CO_3 in the liquid phase and in the position of the newly formed isotherm branch which corresponds to the existence of $K_2CO_3 \cdot 1.5H_2O$ in equilibrium with the liquid phase. The initial solubility of K_2CO_3 increases from 15.00% to 51.28%, while the residual ties for points No. 2, 3, 18, and 19 do not intersect at the figurative point of $K_2CO_3 \cdot 1.5H_2O$ as should be expected for the case of stable equilibrium. Their relative positions indicate the presence of virtual solid phases with variable composition, although actually we have the continuous transition of $K_2CO_3 \cdot 1.5H_2O$ into $K_2CO_3 \cdot 3H_2O_2$ with the probable point for: $K_2CO_3 \cdot 1.5H_2O$, $K_2CO_3 \cdot 3H_2O_2$ with the liquid phase composition of: K_2CO_3 46.0; H_2O_2 17.5; and H_2O 36.5%. The metastable state of the solutions is displaced by the stable state and is noted on the diagram by the branch of points No. 17, 9, 13, 10, 11, and 12, with the solid phase of $K_2CO_3 \cdot 3H_2O_2$. The resulting experimental data for the 0° isotherm of the system $K_2CO_3-H_2O_2-H_2O$ are given in Table 1. Thus, under these conditions we have an interesting case of the presence of both stable and unstable equilibria, in which the stable equilibrium arises in respect to the previously unknown potassium carbonate hydrate.

The existence of the large area of supersaturation shown on the diagram of Fig. 1, enclosed between the isotherm branches for $K_2CO_3 \cdot 1.5H_2O$ and $K_2CO_3 \cdot 4H_2O$, explains the difficulties indicated in the literature describing the experiments with synthetic preparation of $K_2CO_3 \cdot 3H_2O_2$, these difficulties being connected with layer formation in the saturated solutions and with the time of transformation of $K_2CO_3 \cdot 1.5H_2O$ into $K_2CO_3 \cdot 3H_2O_2$. It should be noted, during the consideration of the data for the 0° isotherm for this system, that a strong hydrating effect of hydrogen peroxide relative to $K_2CO_3 \cdot 4H_2O$ exists, along with the sharp increase of solubility of potassium carbonate from 15.00 to 38.24% (point No. 17).

2. 20°C isotherm. The results of the study at 20° are given in Table 2 and are shown graphically in Fig. 2. At 20° the solid phases are the same compounds as at 0°, specifically: $K_2CO_3 \cdot 4H_2O$, $K_2CO_3 \cdot 1.5H_2O$ and $K_2CO_3 \cdot 3H_2O_2$. We determined the location of the branch of stable equilibrium for $K_2CO_3 \cdot 4H_2O$ and that for metastable equilibrium of $K_2CO_3 \cdot 1.5H_2O$.

We were able to extend the study of solubility of 20° up to the content of 38% of hydrogen peroxide in the liquid phase, above which concentration strong decomposition began to set in. The stable branch of crystallization

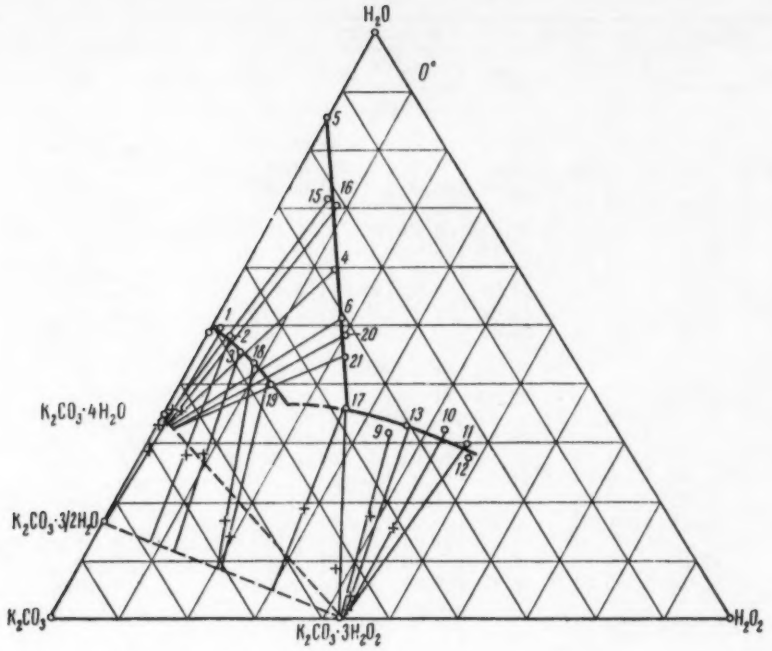


Fig. 1.

TABLE 1

Data on Solubility in the System $K_2CO_3-H_2O_2-H_2O$ at 0°

No. of point	Comp. of liquid phase, wt.%			Comp. of residue, wt. %			Solid phases
	K_2CO_3	H_2O_2	H_2O	K_2CO_3	H_2O_2	H_2O	
				Stable			
5	15,00	0,0	85,00	—	—	—	$K_2CO_3\cdot4H_2O$
15	22,51	6,42	71,07	67,00	—	33,00	$K_2CO_3\cdot4H_2O$
16	21,98	8,75	69,27	64,75	0,90	34,35	$K_2CO_3\cdot4H_2O$
4	27,87	13,33	58,80	63,07	2,48	34,45	$K_2CO_3\cdot4H_2O$
6	30,79	18,83	50,38	65,98	1,40	32,62	$K_2CO_3\cdot4H_2O$
20	31,67	20,83	47,50	65,75	1,25	33,0	$K_2CO_3\cdot4H_2O$
14	32,56	24,58	42,86	—	—	—	$K_2CO_3\cdot4H_2O$
21	33,14	22,43	44,42	62,63	2,41	34,96	$K_2CO_3\cdot4H_2O$
8	34,26	24,29	41,45	—	—	—	$K_2CO_3\cdot4H_2O$
7	33,17	26,35	40,48	52,98	28,69	18,33	$K_2CO_3\cdot4H_2O + K_2CO_3\cdot3H_2O_2$
17	38,24	26,62	35,14	52,72	38,33	8,95	$K_2CO_3\cdot4H_2O + K_2CO_3\cdot3H_2O_2$
9	34,54	34,06	31,40	43,62	39,73	16,65	$K_2CO_3\cdot3H_2O_2$
13	30,96	36,67	32,37	55,26	43,00	1,74	$K_2CO_3\cdot3H_2O_2$
10	25,65	42,84	31,51	41,83	43,14	15,05	$K_2CO_3\cdot3H_2O_2$
11	23,40	47,10	19,50	54,03	42,70	3,27	$K_2CO_3\cdot3H_2O_2$
12	19,87	48,78	31,35	—	—	—	$K_2CO_3\cdot3H_2O_2$
				Metastable			
0	51,28	0,0	48,72	—	—	—	$K_2CO_3\cdot{}^3/_2H_2O$
1	48,95	1,86	49,19	70,33	0,80	28,87	$K_2CO_3\cdot{}^3/_2H_2O$
2	49,32	3,45	47,23	65,35	6,58	24,07	$K_2CO_3\cdot{}^3/_2H_2O$
3	48,96	6,28	44,76	62,24	9,34	28,42	$K_2CO_3\cdot{}^3/_2H_2O$
18	47,70	9,50	42,80	65,73	18,00	16,27	$K_2CO_3\cdot{}^3/_2H_2O$
19	47,12	13,19	38,98	66,29	19,90	13,81	$K_2CO_3\cdot{}^3/_2H_2O$
—	(46,0)	(18,0)	(36,0)	—	—	—	$(K_2CO_3\cdot{}^3/_2H_2O + K_2CO_3\cdot3H_2O_2)$

TABLE 2

Solubility Data in the System $K_2CO_3-H_2O_2-H_2O$ at 20°C

No. of point	Comp. of liquid phase, wt.%			Comp. of residue, wt.%			Solid phases
	K_2CO_3	H_2O_2	H_2O	K_2CO_3	H_2O_2	H_2O	
				Stable			
0	19,01	—	80,99	62,92	—	37,08	$K_2CO_3 \cdot 4H_2O$
9	22,67	3,50	73,83	54,75	1,34	43,91	$K_2CO_3 \cdot 4H_2O$
5	26,17	9,34	64,49	66,00	1,02	32,98	$K_2CO_3 \cdot 4H_2O$
6	30,28	14,27	55,48	61,66	2,82	35,52	$K_2CO_3 \cdot 4H_2O$
17	38,18	23,27	38,55	56,45	36,75	6,80	$K_2CO_3 \cdot 4H_2O + K_2CO_3 \cdot 3H_2O_2$
10	39,10	23,80	37,10	—	—	—	$K_2CO_3 \cdot 3H_2O_2$
7	39,63	24,87	95,50	—	—	—	$K_2CO_3 \cdot 3H_2O_2$
18	40,20	27,12	32,68	56,62	40,98	2,40	$K_2CO_3 \cdot 3H_2O_2$
19	38,70	29,28	32,02	54,36	40,40	5,24	$K_2CO_3 \cdot 3H_2O_2$
20	38,66	31,98	29,36	56,02	40,33	3,65	$K_2CO_3 \cdot 3H_2O_2$
				Metastable			
21	53,84	—	46,16	81,90	—	18,10	$K_2CO_3 \cdot {}^3/_2H_2O$
4	50,70	1,79	47,51	70,70	5,53	23,77	$K_2CO_3 \cdot {}^3/_2H_2O$
11	50,32	3,90	45,78	77,13	2,95	19,92	$K_2CO_3 \cdot {}^3/_2H_2O$
2	48,05	8,78	43,17	76,93	4,15	18,92	$K_2CO_3 \cdot {}^3/_2H_2O$
3	49,90	8,54	41,56	74,32	3,72	21,96	$K_2CO_3 \cdot {}^3/_2H_2O$
12	50,38	8,76	40,86	—	—	—	$K_2CO_3 \cdot {}^3/_2H_2O$
13	49,25	10,49	40,26	—	—	—	$K_2CO_3 \cdot {}^3/_2H_2O$
14	47,25	15,38	37,37	71,04	17,42	11,54	$K_2CO_3 \cdot {}^3/_2H_2O + K_2CO_3 \cdot 3H_2O_2$
15	42,16	19,77	38,07	56,10	39,97	3,93	$K_2CO_3 \cdot 3H_2O_2$
16	40,06	23,17	36,77	56,84	40,27	2,89	$K_2CO_3 \cdot 3H_2O_2$

of $K_2CO_3 \cdot 4H_2O$ has an almost rectilinear form with change of K_2CO_3 solubility from 19.01 to 328.18% at point No. 17, with the solid phases being – $K_2CO_3 \cdot 4H_2O + K_2CO_3 \cdot 3H_2O_2$. The branches of crystallization of $K_2CO_3 \cdot 1.5 H_2O$ (points No. 21, 4, 11, 2, 3, 13, and 14) and $K_2CO_3 \cdot 3H_2O_2$ were determined within the metastable area of the diagram. The transition point No. 14 corresponds to the liquid phase composition: K_2CO_3 . 47.25%; H_2O_2, 15.38%; and H_2O 37.37%; in equilibrium with two solid phases: $K_2CO_3 \cdot 1.5 H_2O$ and $K_2CO_3 \cdot 3H_2O_2$.

3. The −10° isotherm. The data from the study of solubility in the system at −10° are given in Table 3 and are shown graphically in the diagram of Fig. 3. The stable phases in this case, similar to the isotherms which are considered above for 0° and 20°, are $K_2CO_3 \cdot 4H_2O$ and $K_2CO_3 \cdot 3H_2O_2$. The $K_2CO_3 \cdot 6H_2O$ appears as an independent phase only in aqueous solution. Upon introduction of hydrogen peroxide into the liquid phase there arises the metastable phase of $K_2CO_3 \cdot 1.5H_2O$, whose composition varies steadily owing to the progress of a transformation reaction of $K_2CO_3 \cdot 1.5H_2O$ into $K_2CO_3 \cdot 3H_2O_2$. In connection with this fact, the ties of the residues for the isotherm branch (points No. 15, 5, 13 and 14) are displaced and the equilibrium solid phase corresponds to a mechanical

TABLE 3

Solubility Data in the System $K_2CO_3-H_2O_2-H_2O$ at −10°C

No. of point	Comp. of liquid phase, wt%			Comp. of residue, wt.%			Solid phases
	K_2CO_3	H_2O_2	H_2O	K_2CO_3	H_2O_2	H_2O	
				Stable			
0	(15,0)	—	(85,0)	—	—	—	$K_2CO_3 \cdot 4H_2O$
7	16,27	3,20	80,53	58,92	Следы	41,08	$K_2CO_3 \cdot 4H_2O$
9	19,60	9,96	70,44	66,60	»	33,40	$K_2CO_3 \cdot 4H_2O$
3	25,99	14,50	59,51	67,06	0,33	32,61	$K_2CO_3 \cdot 4H_2O$
6	24,65	17,59	57,76	66,36	1,22	32,42	$K_2CO_3 \cdot 4H_2O$
8	26,17	19,27	54,56	65,28	1,86	32,91	$K_2CO_3 \cdot 4H_2O$
10	30,63	25,46	43,91	53,69	18,63	27,68	$K_2CO_3 \cdot 4H_2O + K_2CO_3 \cdot 3H_2O_2$
11	27,52	30,88	41,60	42,34	38,05	19,61	$K_2CO_3 \cdot 3H_2O_2$
12	22,11	43,72	34,17	34,10	41,59	15,31	$K_2CO_3 \cdot 3H_2O_2$
				Metastable			
15	51,12	—	48,88	82,08	—	17,92	$K_2CO_3 \cdot 6H_2O$
5	49,33	6,70	43,97	66,55	16,98	16,47	$K_2CO_3 \cdot {}^3/_2H_2O + K_2CO_3 \cdot 3H_2O_2$
13	48,63	6,77	44,60	73,55	13,04	13,41	$K_2CO_3 \cdot {}^3/_2H_2O + K_2CO_3 \cdot 3H_2O_2$
14	48,38	9,99	41,63	68,82	18,24	12,97	$K_2CO_3 \cdot {}^3/_2H_2O + K_2CO_3 \cdot 3H_2O_2$

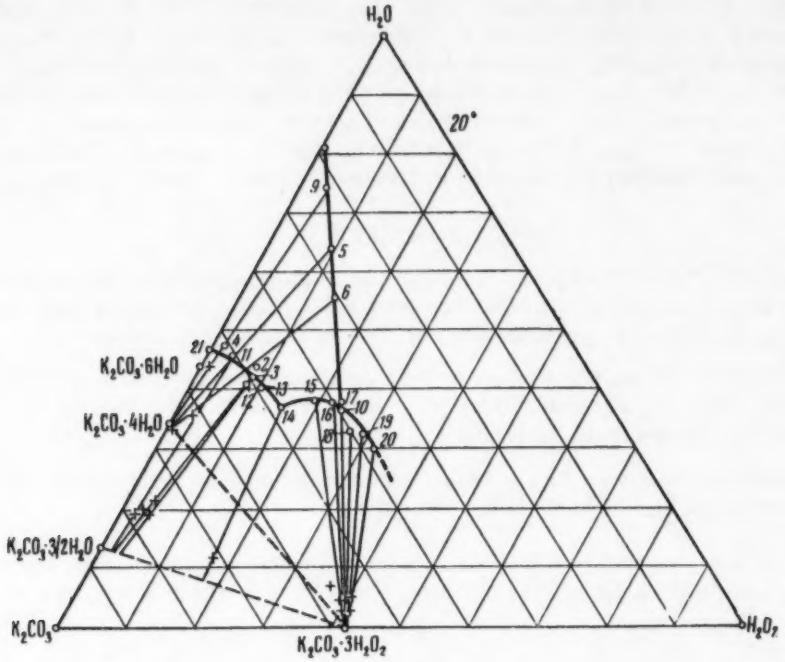

H_2O
20°
$K_2CO_3 \cdot 6H_2O$
$K_2CO_3 \cdot 4H_2O$
$K_2CO_3 \cdot 3/2H_2O$
K_2CO_3
$K_2CO_3 \cdot 3H_2O_2$
H_2O_2

Fig. 2

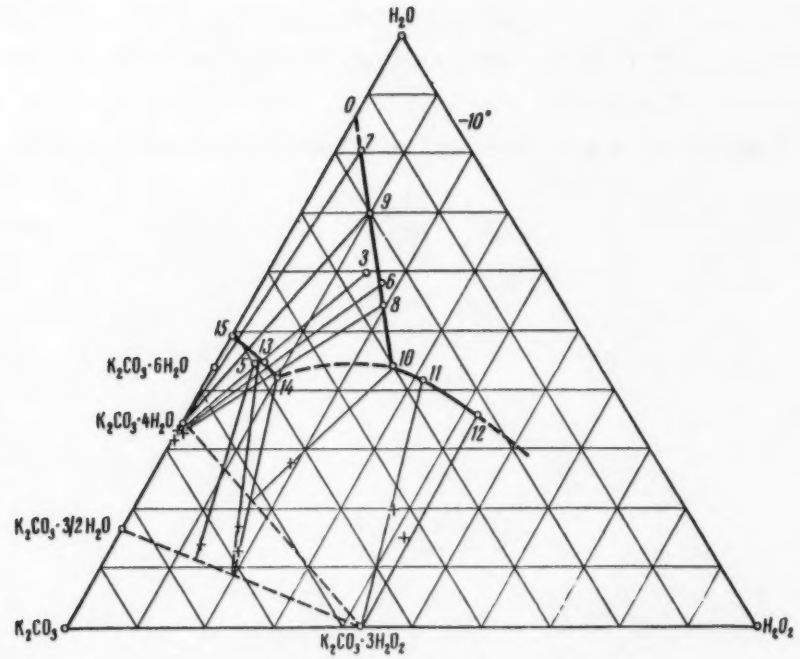

H_2O
0
-10°
$K_2CO_3 \cdot 6H_2O$
$K_2CO_3 \cdot 4H_2O$
$K_2CO_3 \cdot 3/2H_2O$
K_2CO_3
$K_2CO_3 \cdot 3H_2O_2$
H_2O_2

Fig. 3.

mixture of $K_2CO_3 \cdot 1.5H_2O + K_2CO_3 \cdot 3H_2O_2$. The curve (points No. 7, 9, 3, 6, 8, and 10) is the stable branch of the isotherm corresponding to the solid phase $K_2CO_3 \cdot 4H_2O$. The figurative point No. 10 with: K_2CO_3 30.63%, H_2O_2 25.46%, corresponds to the saturation state with two solid phases – $K_2CO_3 \cdot 4H_2O + K_2CO_3 \cdot 3H_2O_2$. The conditions of isolation of the phase $K_2CO_3 \cdot 3H_2O_2$ were traced up to the liquid phase composition of K_2CO_3 22.11% and H_2O_2 42.72% (point No. 12). It is possible to determine the solubility of $K_2CO_3 \cdot 4H_2O$ in water at −10° in 15% potassium carbonate solution by extrapolating the branch of $K_2CO_3 \cdot 4H_2O$ to the region of limitingly low concentrations of H_2O_2 in the liquid phase. The area of concentrations from point No. 14 to point No. 10 (the metastable branch of $K_2CO_3 \cdot 3H_2O_2$) is reproducible only with difficulty and is shown by a dotted line on the diagram of Fig. 3.

SUMMARY

1. The existence of stable solid phases of $K_2CO_3 \cdot 6H_2O$, $K_2CO_3 \cdot 4H_2O$ and $K_2CO_3 \cdot 3H_2O_2$ was established by the study, by means of the solubility method, of the system K_2CO_3–H_2O_2–H_2O at three temperatures: 0, 20 and −10°. Phase $K_2CO_3 \cdot 4H_2O$ is a new, previously unknown, hydrate of potassium carbonate.

2. The equilibrium data permitted us to determine the areas for the solutions of stable concentrations of potassium carbonate and hydrogen peroxide within whose limits it is possible to isolate $K_2CO_3 \cdot 3H_2O_2$ without the phenomenon of layering-out of the liquid phases.

3. Potassium carbonate hydrate $K_2CO_3 \cdot 1.5H_2O$ is the metastable phase in the system and under the action of hydrogen peroxide passes into the stable form $K_2CO_3 \cdot 3H_2O_2$.

4. A sharp increase of solubility with increased content of hydrogen peroxide in the liquid phase is characteristic for the newly found hydrate $K_2CO_3 \cdot 4H_2O$; it changed from 15.00 to 38.24% at 0°.

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A STUDY OF KINETICS OF THERMAL DECOMPOSITION OF SOLID SUBSTANCES

1. THERMAL DECOMPOSITION OF LEAD CARBONATE

O. Kadlets and M. M. Dubinin

Two main methods are used for the study of kinetics of thermal decomposition of solid substances. The first (gravimetric) is based on the direct weighing of the substance undergoing decomposition. In case of the second method (manometric) the kinetics are judged by the time increment of pressure in the vessel which contains the decomposing substance. Both these methods have defects. With gravimetric determinations it is possible to run the thermal decomposition in high vacuum but the supply of heat to the sample, placed on the balance pan, is quite difficult to attain [1] and depends on the pressure in the system which rises with increased degree of decomposition. It is possible to eliminate the defects of the poor supply of heat to the sample by using the manometric method, but in that case the decomposition does not proceed in high vacuum since its rate is estimated by the increase of pressure.

We decided to study the kinetics of thermal decomposition of solid substances by weighing the gaseous reaction products which were adsorbed during the reaction on cooled active carbon. In this manner one may make measurements of low pressures (of the order of 10^{-3} mm of mercury) while maintaining a good supply of heat to the sample.

EXPERIMENTAL

The determination of the kinetics of the thermal decomposition of lead carbonate was made with the apparatus whose diagram is shown in Fig. 1. The decomposition of the specimen was done in the reaction tube 1. The sample was weighed in a glass boat which was placed into tube 2. A piece of iron had been sealed into the boat so that it was possible to dump the boat contents into the reaction tube 1 by means of a magnet. A quartz spiral, to the lower hook of which was hung, by a quartz thread, a pan with 600 mg of microporous activated carbon, was placed in the adsorptional part 3 of the apparatus.

The experiment was run in the following manner. After placing the boat with the specimen sample into the apparatus, the lower end of the adsorption tube 3 was heated to 400° and the apparatus was pumped down to high vacuum. Then the apparatus was disconnected from the vacuum system by stopcock 7 and the lower end of the reaction tube 1 was placed into an electric furnace, preheated to the temperature at which the decomposition of the specimen was to take place. The lower end of the adsorption tube was placed into cryostat 6. We used melting diethyl ether for the cryostatic material. From the instant of dumping of the specimen into reaction tube 1 its thermal decomposition began. The resulting gaseous reaction products (in this case – carbon dioxide) were immediately adsorbed by the cooled activated carbon. The weight of the gaseous reaction products was determined by the weight gain of the activated carbon as established with a cathetometer, and thus it was possible to estimate the degree of decomposition of the specimen with time. In the study of decomposition kinetics for such substances whose decomposition products may be nitrogen, oxygen or carbon monoxide it is necessary to cool the activated carbon with liquid nitrogen.

It was proved, prior to the systematic measurements, that the rate of adsorption of the gaseous reaction products was many times greater than the rate of thermal decomposition of the specimen. For this purpose we sealed a stopcock at location 4 in the connecting tube of the apparatus so as to enable us to isolate the adsorptional part

of the apparatus from the part in which the decomposition took place.

If the rate of adsorption of the gaseous reaction products under the experimental conditions were insufficiently great, we should have observed for a period of some time a weight gain of the activated carbon after closing stopcock 4 during a run of the thermal decomposition of a specimen. However, this additional adsorption was not detected at even very great rates of decomposition of the specimen. The results of measurements and, specifically, the independence of the decomposition curves from the size of the specimen samples indicate that the rate of adsorption of the gaseous reaction products was sufficiently high; this is shown especially by the coincidence of the kinetic constants for three independent measurements with specimens having different magnitudes of grain surface areas.

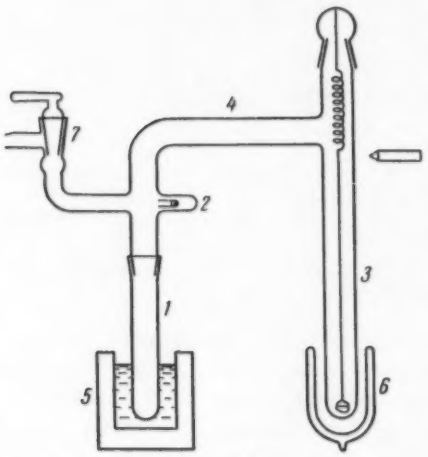

Fig. 1. Diagram of the apparatus.

The kinetics of thermal decomposition of cerucite, which is pure lead carbonate, was investigated in detail by means of the apparatus described above. The cerucite crystals were ground in an agate mortar and were separated over three narrow fractions with various grain dimensions by means of appropriate sieves. The measured curves of the thermal decomposition for one of the fractions of grains of the lead carbonate sample are shown in Fig. 2 for the temperature interval of 100°, as an example. The high order of dependence of the rate of decomposition of lead carbonate on temperature should be noted.

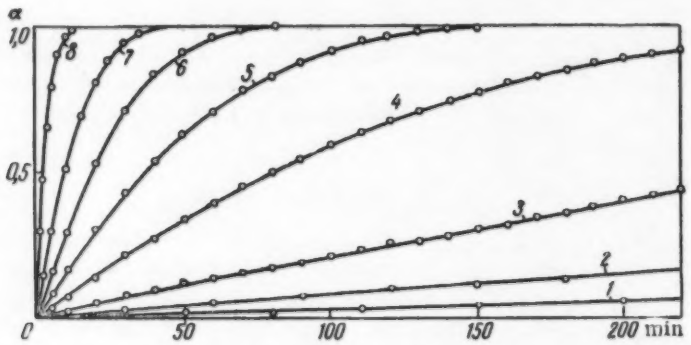

Fig. 2. Dependence of degree of decomposition of lead carbonate on time at temperatures from 236 to 335° for the most disperse fraction III: 1) 236°; 2) 245°; 3) 260°; 4) 280°; 5) 290°; 6) 300°; 7) 310°; 8) 335°.

Discussion of the Experimental Results

The results of the measurement of the kinetics of thermal decomposition of three grain fractions satisfied well the equation which was derived on the basis of an assumption that the rate of decomposition of a solid is directly proportional to the surface of the substance [2]. This supposition may be expressed by the equation:

$$-\frac{dm}{dt}=kS, \tag{1}$$

where S is external surface of the specimen grains; m is its mass; k is the kinetic constant which depends only on temperature for a given sample.

If n is the number of grains in a specimen sample, the assumption of spherical form of the grains leads to the summary area of all grains being equal to:

$$S = n4\pi r^2, \tag{2}$$

where r is the radius of grains of the given fraction, which is determined by the conditions:

$$n\frac{4}{3}\pi r^3 = \frac{m}{\rho}, \tag{3}$$

where ρ is the density of the substance. It is therefore possible to express Equation (1) in the form:

$$-\frac{dm}{dt} = kn^{1/3}4\pi\left(\frac{3}{4\pi}\right)^{2/3}\frac{1}{\rho^{2/3}}m^{2/3}. \tag{4}$$

By integration of this equation we obtain:

$$m^{1/3} = m_0^{1/3} - Kt, \tag{5}$$

where m_0 is the mass of the specimen at the beginning of the experiment and constant K is equal to:

$$K = 1{,}61\frac{n^{1/3}}{\rho^{2/3}}k. \tag{6}$$

If the assumption of direct proportionality of the rate of thermal decomposition to the surface area of the undecomposed substance is valid, one should observe according to Equation (5) a linear dependence between the cubic root of the mass of undecomposed substance and time t. The tangent of the angle of slope of these curves is equal to the constant K. This linear dependence was observed in all cases for the entire region of decomposition. For an example we give in the graph of Fig. 3 the relation of the cubic roots of the weight of as yet undecomposed substance at time t to the time t for a temperature interval from 236 to 335° for the most fine grain fraction III. Similar lines were obtained for the remaining two fractions.

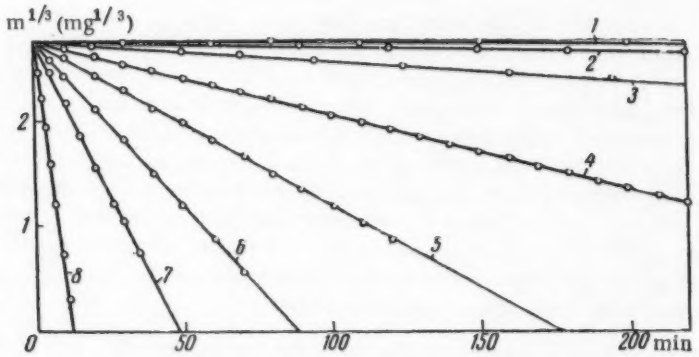

Fig. 3. Dependence of cubic roots of the masses of undecomposed substance on time, for temperatures from 236 to 335° (fraction III): 1) 236°; 2) 245°; 3) 260°; 4) 280°; 5) 290°; 6) 300°; 7) 310°; 8) 335°.

The dependence of the logarithms of the calculated constants K on the reciprocals of absolute temperatures is shown in Fig. 4 where it appears expressed by straight lines with the same slope. From the angle coefficients of these lines we calculated the activation energy E of the thermal decomposition of lead carbonate, which turned out to be 41,500 calories per mole. The kinetic constants k

$$k = \frac{2{,}15}{n^{\frac{1}{3}}} K. \qquad (7)$$

were calculated with Equation (6) from the measured constants K, the number of grains in the sample, and the density of the specimens ρ, which was equal to 6.45 mg/cm^3.

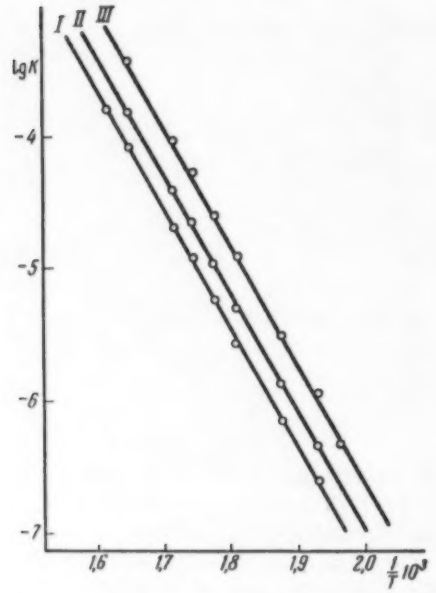

Fig. 4. Dependence of logarithms of kinetic constants K on reciprocals of absolute temperatures for fractions I, II and III.

The results of the calculations are given in the table for the various temperatures used. The coincidence of the constant $\underline{k}$, calculated from three independent measurements with different grains fractions, was good. The activation energy of thermal decomposition of lead carbonate, calculated from the mean values of kinetic constants $\underline{k}$ for each temperature, was also equal to 41,500 calories per mole. Therefore, the kinetic constant $\underline{k}$ may be expressed as:

$$k = Ae^{-\frac{E}{RT}}. \qquad (8)$$

The values of the pre-exponential factor A were calculated from the measured values of constants $\underline{k}$ and the activation energy E. The mean value of the pre-exponential factor A, calculated for nine different temperatures in the interval from 236 to 345°, was equal to $5.0 \cdot 10^{10}$ grams per square centimeter per second. Thus, the kinetics of thermal decomposition of lead carbonate is determined by only two constants – activation energy E and the pre-exponential factor A.

The results obtained in the study of the kinetics of thermal decomposition of lead carbonate are also interesting from the point of view that the decomposition proceeded with maximum rate from the very beginning of the process, in contrast to experiments by Centnerszwer and Awerbuch [3] who observed a seven-minute induction period. The activation energy of thermal decomposition of lead carbonate, E = 41,500 calories per mole as measured in our work, differs considerably from the value found by Bruzs [4] of 69,600 calories per mole. Centnerszwer and Awerbuch, as well as Bruzs, expressed the rate of decomposition of lead carbonate by an equation for a monomolecular reaction. In view of the good agreement of the kinetic constants $\underline{k}$, calculated from measurements on fractions with different grain size, the results obtained in our present work are more dependable than are the results of the authors cited above. These results are also more dependable since, in contrast to the cited papers, in which the decomposition was never carried to completion, the decomposition proceeded practically to completion in our present work since the experiments were run in sufficiently high vacuum; this was true in all cases, and even at the lowest temperatures. It follows clearly from the results obtained by us that the reaction occurs over the entire surface of the specimen, during the decomposition of lead carbonate, without any autocatalytic action of the solid reaction product, with the reaction rate being directly proportional to the surface area of the undecomposed specimen.

The new method of study of the kinetics of thermal decomposition of solids, used in this work, is the more dependable one. It is possible to measure the decomposition at the lowest pressure by using a suitable activated carbon and a rational method of cooling it. At the same time it is possible to maintain a constant temperature of the sample directly from the instant the decomposition begins. The apparatus may be used in such cases in which the other methods are inapplicable. If two substances are being subjected to decomposition at the same time and these yield different gaseous products as the result of the reaction, it is possible to measure the rate of only one of the reactions. By suitable cooling it is possible to attain the conditions under which the activated carbon would absorb only one of the gases while the other would be condensed on the walls of a trap, cooled to a

Kinetic Constants of the Reaction of Thermal Decomposition of Lead Carbonate

Temp. in °C	Fraction	n	K in $gm^{1/3}/sec$	k [$gm/sec \cdot cm^2$]	
236	III	2930	$4,63 \cdot 10^{-7}$	$6,95 \cdot 10^{-8}$	
245	I	36	$2,54 \cdot 10^{-7}$	$1,66 \cdot 10^{-7}$	
	II	202	$4,64 \cdot 10^{-7}$	$1,69 \cdot 10^{-7}$	$1,68 \cdot 10^{-7}$
	III	2930	$1,13 \cdot 10^{-6}$	$1,70 \cdot 10^{-7}$	
260	I	36	$6,34 \cdot 10^{-7}$	$4,52 \cdot 10^{-7}$	
	II	202	$1,39 \cdot 10^{-6}$	$5,08 \cdot 10^{-7}$	$4,78 \cdot 10^{-7}$
	III	2930	$3,45 \cdot 10^{-6}$	$4,73 \cdot 10^{-7}$	
280	I	36	$2,78 \cdot 10^{-6}$	$1,81 \cdot 10^{-6}$	
	II	202	$5,09 \cdot 10^{-6}$	$1,86 \cdot 10^{-6}$	$1,83 \cdot 10^{-6}$
	III	2930	$1,20 \cdot 10^{-5}$	$1,81 \cdot 10^{-6}$	
290	I	36	$5,78 \cdot 10^{-6}$	$3,77 \cdot 10^{-6}$	
	II	202	$1,06 \cdot 10^{-5}$	$3,89 \cdot 10^{-6}$	$3,83 \cdot 10^{-6}$
	III	2930	$2,54 \cdot 10^{-5}$	$3,82 \cdot 10^{-6}$	
300	I	36	$1,20 \cdot 10^{-5}$	$7,83 \cdot 10^{-6}$	
	II	202	$2,22 \cdot 10^{-5}$	$8,13 \cdot 10^{-6}$	$7,98 \cdot 10^{-6}$
	III	2930	$5,32 \cdot 10^{-5}$	$7,99 \cdot 10^{-6}$	
310	I	36	$2,13 \cdot 10^{-5}$	$1,39 \cdot 10^{-5}$	
	II	202	$3,89 \cdot 10^{-5}$	$1,42 \cdot 10^{-5}$	$1,41 \cdot 10^{-5}$
	III	2930	$9,48 \cdot 10^{-5}$	$1,42 \cdot 10^{-5}$	
335	I	36	$8,33 \cdot 10^{-5}$	$5,42 \cdot 10^{-5}$	
	II	202	$1,57 \cdot 10^{-4}$	$5,76 \cdot 10^{-5}$	$5,58 \cdot 10^{-5}$
	III	2930	$3,70 \cdot 10^{-4}$	$5,56 \cdot 10^{-5}$	
345	I	36	$1,62 \cdot 10^{-4}$	$1,05 \cdot 10^{-4}$	

lower temperature and placed in front of the adsorption tube.* Thus, it is possible, for example, to measure the rate of thermal decomposition of silver oxide formed directly by the decomposition of the carbonate. If the trap is cooled with liquid nitrogen, the carbon dioxide gas – the decomposition product of the carbonate – would be totally condensed on the cooled walls of the trap while oxygen, formed by the decomposition of silver oxide, would be practically completely adsorbed by the activated carbon. It is possible to use this method in those cases in which two decompositions overlap each other. The end of dehydration of various substances is often overlapped with the beginning of their further decomposition. It will be possible now to study the rate of decomposition of a substance even during the time of its dehydration, by condensation of the water vapors on the cooled trap walls.

In conclusion, the authors consider it their pleasant duty to express their gratitude to Assistant Z. Gauptman for his aid in completing the work and for the discussion of the results obtained.

SUMMARY

1. A new method of study of the kinetics of thermal decomposition of solids, which permits one to accomplish the process in vacuum with a good heat supply to the specimen, was developed in this work.

2. Decomposition of lead carbonate occurs at a rate which is proportional to the surface area of the undecomposed substance without any autocatalytic action of the solid reaction product.

3. The activation energy of thermal decomposition of lead carbonate and the pre-exponential factor were calculated. The value of the activation energy was found to be 41,500 calories per mole while the values of the pre-exponential factor was $(0.5 \pm 0.5) \cdot 10^{10}$ $gm/cm^{-2} \cdot sec^{-1}$.

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A STUDY OF THE STRUCTURE OF TITANIUM DIOXIDE GELS BY INDEPENDENT METHODS

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Titanium dioxide gels have appreciable adsorptional [1] and catalytic [2] properties. Among the reactions catalyzed by these gels are: dehydrogenation of cytoparaffins, condensation of acetylene with water, methane and aromatic hydrocarbons, dehydration and dehydrogenation of alcohols, etc. The nature of the porosity of the catalyst has an influence on the operation of the latter, in addition to the effect of the chemical composition. The effective operation of the catalyst depends on the correct combination of external conditions with the internal grain structure. For reactions which proceed at high speed the inner surface of finely porous catalysts is likely to be difficultly accessible. The character of the porosity of the catalyst may also affect not only the rate but also the direction of the process [3]. Owing to this, the problem of a rational application of porous adsorbents and catalysts presents to the workers a series of questions, among which the important ones are: the development of scientifically based methods of reproducible preparation of adsorbents and catalysts with a given porous structure and the multilateral study of the skeleton structure of these materials.

Only the dependence of the catalytic and the adsorptional properties of titanium gels on the conditions of their preparation is supplied in the few papers which bear on the study of the structure of these gels [4]. The porous structure of titanium dioxide gels was not studied in these publications. It was of interest to make a complex study of titanium dioxide gels with different porous stuructures making use of various methods for the collection of more diverse condepts of the gel structure and for the determination of the limits of applicability of the several methods. We used independent methods for this study and the work was done jointly by the Institute of Physical Chemistry of the Academy of Sciences of Ukrainian SSR (preparation of titanium dioxide gels of different structures and the adsorptionally structural studies) and by the Institute of Physical Chemistry of the Academy of Sciences of the USSR (electron microscopic, x-ray and electronographic studies).

EXPERIMENTAL

Preparation of specimens of the titanium dioxide gels. In the preparation of the titanium gels with differently porous structures we were guided by the theoretical concepts of the mechanism of the formation of the structure of hydrophilic sorbents, developed by Neimark and his co-workers [5]. According to these concepts, an important role is played in the formation of the structure of hydrophilic sorbents by capillary forces which depend, on the one hand on surface tension of the intermicellar fluid and the degree of wetting of the capillary walls by the fluid, and on the other hand, on the degree of aggregation of the particles into chains or clusters during the process of gel ripening.

The preparation of the specimens was done as follows. To 4 liters of N ammonium hydroxide solution there was added, dropwise and with energetic stirring, 25 ml of titanium tetrachloride solution. The precipitate of titanium hydroxide was left in contact with the mother liquor for varying periods (Table 1) after which it was washed with distilled water until the chloride ion test became negative. Samples 1-3 were dried at first at 20°, then at 110°. Replacement of the intermicellar fluid (water) by n-butyl alcohol in the hydrogel precipitate was performed in the preparation of specimen 4. After repeated treatment of the titanium dioxide gel with n-butyl alcohol, the specimen was dried on a water bath.

Adsorption structure measurements. Absorption-desorption isotherms were determined at 20° for each of the specimens of titanium dioxide gels with methyl alcohol vapors. In addition, we determined the total pore volume by the difference between the reciprocals of the values of apparent and actual densities, and the static activity in respect to benzene in the atmosphere of the saturated vapor. The values of the specific surfaces were calculated from the sorption isotherms by the B.E.T. method, with the magnitude of the area occupied by a methanol molecule in a dense monomolecular layer being taken as 25 square Angstroms. The sorption isotherms of methyl alcohol vapors for various specimens are given in Figs. 1 and 2, while the structurally sorptional characterization of the titanium dioxide gels studied by us is given in Table 1.

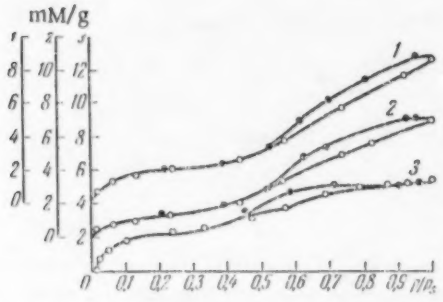

Fig. 1. Adsorption isotherms of methyl alcohol vapors on specimens 1-3 of finely porous titanium gels (black dots – desorption).

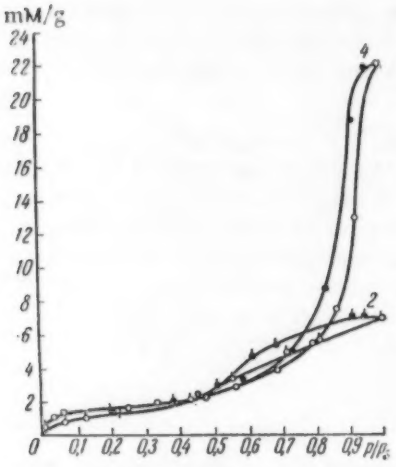

Fig. 2. Adsorption isotherms of methyl alcohol vapors on titanium gels: macroporous No. 4 and finely porous No. 2 specimens (black dots – desorption).

It follows from the graphs and the data in the table that the titanium gels prepared by us had different porous structures, depending on the conditions of their preparation. Specimens 1-3 belong to the category of the finely porous ones. The apparent specific gravity of these titanium gels increases with increased duration of ripening while the limiting sorptional volume decreases. Therefore, a constriction of the gel skeleton occurs during the stay in the mother liquor. On the contrary, specimen 4 is a macroporous sorbent whose summary pore volume reaches 0.84 cc/g. This is caused by the replacement of its intermicellar fluid – water – by a liquid with a lower surface tension. The difference in the porous structures of the macroporous and the finely porous gels is clearly seen in Fig. 2, where we give the isotherms for specimens 2 and 4.

Electron-microscopic study. We used the replica method for the electron-microscopic study since it permitted the observation of the undisturbed structure of the sorbents. The replicas were made from the fresh surface of a cleavage of pressed granules of the gels, while both collodion and carbon replicas were used at first for control and comparison.

The collodion replicas were prepared by deposition of a drop of 0.01% collodion solution in amyl acetate on the surface of the specimen; the excess solution was then picked up with filter paper. The specimen was stored for about one day in order to evaporate the solvent and to complete the film formation, after which the specimen was dissolved in a concentrated solution of hydrofluoric acid. The separated collodion replica was washed thoroughly, dried and shaded with platinum.

In order to form the carbon replicas we deposited on the gel surfaces a thin layer of carbon by thermal evaporation of the latter from the spot of contact of two spectrographically pure graphite rods heated by electric current. The current strength used was up to 20 amperes at 2 volts; the evaporation time was 10-15 seconds. The separation and the treatment of the carbon replicas were done similarly to the collodion replicas. In some cases a contrasting layer of platinum was first deposited on the specimen, followed by a carbon film. There are indications in the literature that this procedure at times gives a better resolution on photographs than the usually employed method – shading of the finished films.

For preparation of thin films which would assure an image of good quality we employed the preliminary fastening of the replicas and a number of other techniques which had been described in paper [6]. The photography was done with the UEM-100 electron microscope at magnification of 14,000. The focusing was done with a binocular lens which gave a 20-fold magnification.

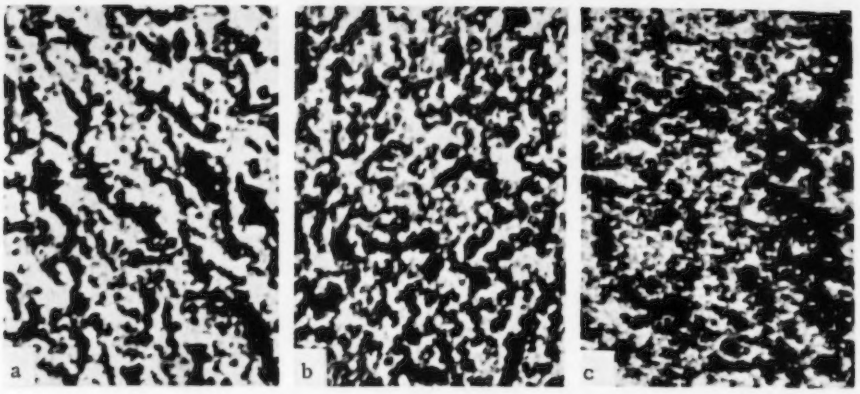

Fig. 3. Replicas from macroporous (specimen No. 4) of titanium dioxide gel: a) collodion; b) carbon; prepared by shading of a carbon imprint with platinum; c) carbon; prepared by first depositing a contrasting layer of platinum onto the gel, followed by deposition of a carbon film (× 60,000).

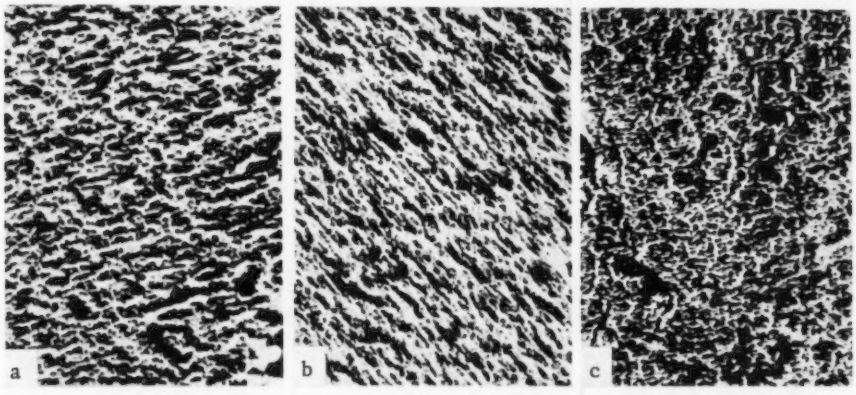

Fig. 4. Carbon replicas, contrasted with platinum, taken from finely porous gels of titanium dioxide: a) specimen No. 1; b) specimen No. 2; c) specimens No. 3 (× 60,000).

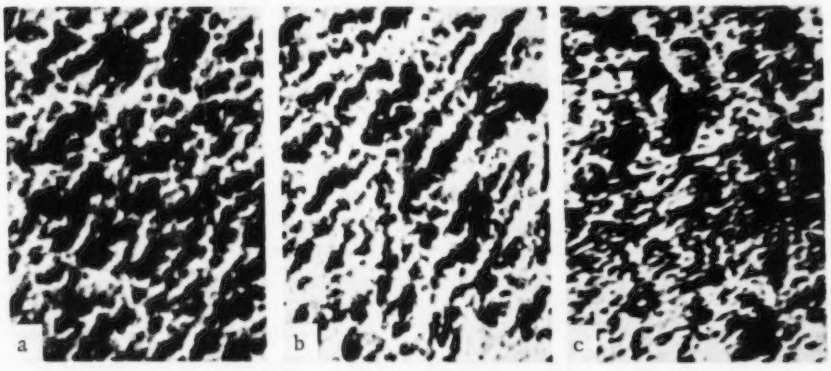

Fig. 5. Same as on Fig. 4 but at greater optical magnification: a) specimen No. 1; b) specimen No. 2; c) specimen No. 3 (× 180,000).

TABLE 1

Structural Characterization of Titanium Gels

Sample No.	Duration of ripening in hours	Apparent specific gravity in g/cc	V_Σ in cc/g	Static activity relative to benzene in %	Limiting sorptional volume in cc/g		Specific surface area from B.E.T. formula in m^2/g	Effective radius of the pores, from distribution curve, in A	Electron microscopic data (approximate)	
					C_6H_6; desiccator method	CH_3OH; from isotherm			mean particle diameter in A	geometric specific area in m^2/g
1	0	1,53	0,34	30,0	0,34	0,35	291	12,5	—	—
2	3	1,68	0,28	24,5	0,28	0,28	234	22,5	60	260
3	120	1,82	0,24	20,0	0,23	0,21	285	12,5	60	260
4	Replacement of intermicellar liquid	0,90	0,80	74,7	0,85	0,88	214	47,5	80	190

Let us consider the results obtained by us. It follows from Fig. 3, on which we show the photographs of the various replicas from the same specimen of a macroporous gel, that this specimen has a globular structure. Particles, with a form that is close to spherical, make up the skeleton of the gel, as is clearly visible on the reproduction. Although a structure of the same character is seen on all the photographs, a comparison of the photographs shows the advantage of the carbon replicas; the resolution is better with them and this permits one to distinguish smaller particles. This is explained by the fact that the formation of the carbon replicas occurs under more favorable conditions by condensation of atomic (or nearly so) clusters of carbon on the surface that is being studied, while in the case of the collodion replicas the smoothing of the original relief on the final imprints is much more probable during the drying of the film-forming solution. Therefore the accumulations of particles, each of which is individually discernible on the carbon replicas, often appear as solid formations on the collodion replicas. The smallest visible particles are seen in Fig. 3c.

The study of the finely porous gels was done exclusively with the carbon replicas since the collodion replicas turned out to be totally unsatisfactory. These gels have a rather highly dispersed structure that is similar for all three specimens, as it is evident in Fig. 4. The apparent orientation of the structure in Fig. 4b is probably explained by the shading effect.

Based on these photographs we may draw a qualitative conclusion to the effect that the finely porous gels have a relatively compact structure, that the proportion of free space within them is smaller than in the macroporous gel (Fig. 3). This agrees with the data concerning the apparent specific gravity of the specimens studied by us (Table 1).

A diligent examination of the negatives in a projector at high magnifications indicates that the finely porous gels of specimens No. 2 and 3 also consist of particles of very small dimensions which are coupled together in threads. One may obtain an idea of this structure from Fig. 5 where we show the photographs of the finely porous gels at very high magnification which exceeds the useful magnification limits in the optical sense in order to avoid material distortions in the reproduction of these prints for the press. For specimen No. 1 (Fig. 5a) which was not kept for ripening we could not detect any particles of sufficiently definite form, in contrast to the other gels.

On photograph negatives of specimens No. 2, 3 and 4, in which one may distinguish the individual particles, we determined the mean dimensions of the particles by measuring them with a projector. Usually the images of the particles appear as elongated oval spots. This may be caused both by the sticking of the individual particles into threads and by the effect of shading in the preparation of the replicas [7]. Therefore, during the measurements we evaluated the smaller, transverse dimension of the particle images. The rounded mean dimensions of the particles for the finely porous gels were found to be equal to 60 A, while for the coarsely porous gel this was 80 A (see Table 1).

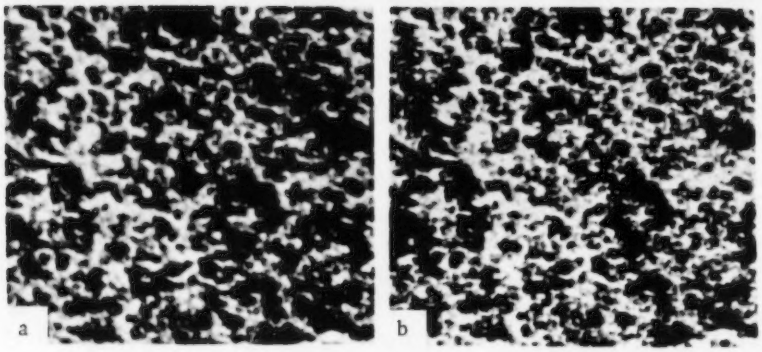

Fig. 6. Stereo-pair of a replica from macroporous titanium dioxide gel. The replica was prepared by at first depositing on the gel a contrasting layer of platinum, followed by a carbon film. (× 60,000).

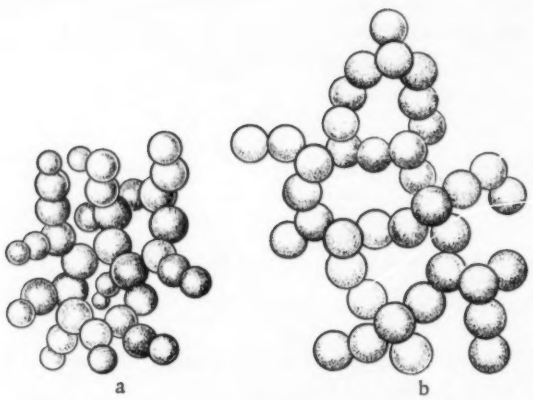

Fig. 7. a, b) A schematic representation of the structure of individual regions of the macroporous gel of titanium dioxide from stereoscopic data.

It must be noted that the data given above on the particle dimensions should be considered as orienting or preliminary ones. The resolving power of the electron microscope was 30 A and the question of the accuracy with which one could measure objects whose dimensions exceeded the resolving power of the instrument only by two or three-fold remains basically unanswered. This question has not been clarified theoretically and requires a special study. We shall only note in this connection that there is basis to suppose that in the determination of mean particle dimensions one would make an error that is smaller than the value of the resolving power of the microscope. Some additional difficulties arise in connection with the fact that in our case we examined the replicas from the particles and not the particles themselves. This could introduce some new errors since the accuracy of the replica method in studying such small objects has not been evaluated sufficiently. However, there exists a paper in which the accuracy of the replica method was checked quantitatively on nonporous particles of silicon dioxide with diameter of about 100 A. A comparison of the distribution curves of the particles according to the dimensions obtained by measurements of the particles on photographs and of the carbon replicas taken from them permitted an evaluation of the error in the replica method at 10% for this region of dimensions [7]. It appears to us, therefore, that the error in the determination of the particle dimensions in gels of titanium dioxide would hardly exceed 20-30% and it is very improbable that it could reach 50%.

We succeeded in obtaining some additional data on the structure of the macroporous gel by means of stereoscopy. We show one of the stereophotographs studied by us in Fig. 6 as an example. Here one may examine the individual particles more clearly and, what is more interesting, one may secure an idea of their spatial disposition and bonding. It is apparent on these stereophotographs that the gel has a rather loose structure and that a considerable part of the volume is occupied by voids. The presence of chains, consisting of contiguous particles, is characteristic, while often these chains form closed rings with an open inner space (Fig. 6, right top). In other locations the particles form agglomerations which resemble grape clusters which are, however, packed but loosely. On the average the coordination number for this system is probably close to three or four. One must keep in mind that here we may observe not the entire structure of the upper layers of the gel but only the separate, more or less complete, fragments of it. This is first of all due to the conditions of the preparation of the carbon replica – only those regions of the structure are visible which are accessible to the carbon particle ray which

propagates rectilinearly and regions which are contrasted with platinum as well. Nevertheless, one does obtain a good stereo-effect in individual locations and one can see some details of the gel structure within its depth which corresponds approximately to ten or more particle diameters. This fact itself shows the loose packing of the particles in the gel; usually one can observe only the very uppermost layer of particles in stereophotographs of silica gels, for example, where a dense packing occurs.

Based on the study of a number of stereophotographs, we attempted to reproduce schematically the structure of what appeared to us the characteristic regions of the gel which we discussed above (Fig. 7). These schemes are close to those given in Manegold's article [8] for the proposed structures of gels formed by contiguous spherical particles with coordination number of 3 and 4.

We failed to get a sufficient stereo-effect in photographs of the replicas from the finely porous gels. This was evidently connected with the small dimensions of the particles and with the denser packing owing to which the surface of a cleft is relatively smooth, approaching that formed by silica gels. In addition to this, the magnitude of the angle at which the atomic rays of carbon and platinum are directed onto the gel surface during the preparation of the replicas also has a significance. This angle should not be too small since the ray which grazes the surface cannot penetrate the deeper layers of the sample.

Results of x-ray and electronographic studies. We took the x-ray diffraction patterns of gel samples No. 3 and No. 4 with Cu$-K_\alpha$ radiation. We failed to obtain a diffraction pattern for sample No. 3. From sample No. 4 we obtained some sufficiently clear diffraction lines, which were somewhat widened, this fact speaking of a finely crystalline structure. The results of the measurements of the interplanar distances on the x-ray pattern from sample No. 4 are given in Table 2, in comparison with the reference data for anatase (d_{table}).

TABLE 2

Results of Roentgenographic Analysis of Sample No. 4 of Titanium Gel

sin ϑ	0,219	0,323	0,403	0,452	0,515	0,566
d_{expt} kX	3,53	2,38	1,90	1,70	1,49	1,36
d_{table} kX	3,52	2,37	1,88	1,70	1,48	1,36

It follows from the data in Table 2 that sample No. 4 has the crystalline structure of anatase. The electronographic study of samples No. 1, 2 and 3 showed that these have an amorphous structure.

These results do not contradict the literature data. Thus in paper [9] it was shown by x-ray structural analysis that the precipitates of titanium dioxide prepared from solutions of titanium chloride and sulfate at room temperature are amorphous. The precipitate turned into anatase on being heated to 300°.

Discussion of the Results Obtained

The purpose of a complex study, in which the same objects are examined by different methods, should be the comparison of the results of these methods for the development of a broader understanding of the structure of the substance and, also, for mutual check of the methods.

The electron microscopic examination permitted us to establish the globular structure of titanium dioxide gels and to evaluate the globule dimensions. It is natural to attempt to calculate from these results the magnitudes of the specific geometric areas and to compare the data thus obtained with the adsorptional data. For this it is necessary to know the density of the material of the specimens. Since the macroporous gel has the structure of anatase, it is possible to take the value of its density, equal to 3.84, into the calculation. On the basis of the photographs, especially the stereoscopic ones, one may regard the shape of the particles as being spherical. From this the magnitude of the specific geometric surface of the gel becomes approximately equal to 190 square meters per gram. The finely porous gels are amorphous, by the electronographic and x-ray data, and the magnitude of their density is unknown. If we take their density to be equal to 3.84 also, this should not lead to a large error, in our opinion, and this value yields the specific geometric surface area of approximately 260 square meters per gram for a spherical form of the nonporous particles.

The magnitudes of the specific surfaces, calculated from the data of both methods, are compared in Table 1. A good agreement of the calculated values is observed for samples No. 3 and 4, while for sample No. 2 the size of the specific area calculated from electron microscopic pictures exceeds that calculated from the adsorptional data by 27% (260 and 204 square meters per gram, respectively). The specific area was not calculated from the electron microscopic data for sample No. 1 since no particles with sufficiently clear form were detectable in the photographs.

It should be noted that errors may arise from two factors during the calculation of the specific surface of bodies with globular structure from electron microscopic data even when the particles have a truly spherical form and we have exact knowledge of their dimensions and density. The electron microscopic method is incapable, on one hand, of determining the possible microporosity or roughness of the surface of the particles themselves and, on the other hand, of evaluating sufficiently accurately the fusion of the particles at the sites of their contact. These two factors operate in different directions in the sense of their effect on the magnitude of the specific surface of a given body that is being calculated and they compensate each other to some degree. The situation is simpler if the particles, in the main, preserve their individuality, as is the case for some forms of carbon black. For this reason carbon blacks were included in the standard samples during a complex study in paper [10] which showed that in the large majority of cases the adsorptional and the electron microscopic methods and the small angle scattering method for x-rays give results in good agreement as to the dimensions of amicroscopic particles.

The stereophotographs of the macroporous gel indicate that the particles which compose this gel are spherical and that they preserve their individuality to a considerable degree in the loose packing of the gel. Hence it follows, from the fact of the close agreement of the specific surface areas of the gel calculated by both methods, that its particles are nonporous. The same conclusion can be drawn for samples No. 2 and 3, although with less foundation. The circumstance that the geometric specific surface of sample No. 2 exceeds the adsorptional surface denotes the absence of porosity in the particles of this specimen.

Thus, for a first approximation, the gels of samples No. 2, 3 and 4 may be regarded as being composed of nonporous particles with spherical form and the spaces between the particles must be the pores. This allows us to provide a qualitative explanation for the different character of porosity of the gels as sorbents. Sample No. 4 is constructed from the relatively loosely packed, larger particles, which defines its character as a relatively macroporous specimen in the series under study. The finely porous gels No. 2 and 3 are formed from smaller and more densely packed particles which provides the smaller effective pore dimensions, as calculated from the theory of capillary condensation, as well as the smaller limiting volume of the sorptional space.

The concepts of the possible globular gel structure, specifically of silica gels, have existed for a long time (see for example [11]). These concepts were applied by Kiselev to the development of the theory of sorption of vapors in the bodies with corpuscular structure, while some sorptional data were obtained which confirmed the existence of such structures [12]. Independent proofs of the globular structure of silica gels [7] and aluminosilicate catalysts [13] were obtained recently by means of the electron microscope. Thus, results showing the globular structure of titanium dioxide gels is not unexpected; on the contrary, one should expect that the further use of electron microscopy will allow us to ascertain the globular structure of a number of other gels.

In conclusion, let us attempt to review the formation of the structure of titanium dioxide gels. A hydrosol of titanium dioxide is formed on mixing solutions of titanium tetrachloride and ammonia. The particles of this hydrosol are probably amorphous and have a spherical form [14]. With passage of time these particles collect in chains and aggregates, forming a hydrogel. Depending on the conditions of ripening and dehydration of the gel, this aggregation proceeds differently. During the dehydration of the gel under the condition of low magnitudes of the capillary forces, the packing of the particles will be loose and the gel will be formed in macroporous form. A sharp contraction of the gel volume occurs during the drying of hydrogels (water being the intermicellar fluid) owing to the development of quite large area of the demarcation of liquid-gas at which large forces of surface tension operate and tend to contract the dimensions of the resulting pores with maximum approach of the gel particles. Finely porous samples would form as the result. Consequently, the skeleton of the finely porous titanium gel should consist of densely packed particles of titanium dioxide while the main bulk of the pore volume should consist of the volume of the voids located between the particles.

SUMMARY

1. An adsorptional and an electron microscopic study of a series of samples of titanium dioxide gels, prepared by hydrolysis of titanium chloride, was made. The comparison of the results from both methods allowed us to obtain a more complete picture of gel structure.

2. The gels are constructed from spherical particles which, as the first approximation, may be regarded as being nonporous. The values of the specific surface areas of the gels are mainly determined by the particles dimensions while the character of the porosity is determined by the dimensions and the density of their packing. The pores should be regarded as the spaces between the contacting particles.

3. Replacement of water in hydrogels by liquid with a lower surface tension allows one to obtain sorbents with larger and less densely packed particles. Such gels are relatively macroporous in the adsorptional sense. The lengthening of the ripening period for titanium dioxide hydrogels in the mother liquor reduces the porosity of the specimens due to the realization of denser packing of the particles in the sorbents.

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CONCERNING THE NATURE OF THE MAXIMUM IN THE ISOBARS OF HYDROGEN ADSORPTION ON NICKEL, PLATINUM, IRON, CHROMIUM AND OTHER METALS

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Studies of hydrogen adsorption on Ni, Fe, W and Pt made in the 30's and 40's [1-16] and recently [17-26] showed that the adsorption increases with the rise in temperature from −195° to −78° − 0°, then decreases from 0° to 50° or higher, i.e., that the adsorption isobars have a maximum between −78° and 0° (or −50°). Some workers have found the existence of even two maxima [5, 13]. The increase of the summary adsorption and the maximum in the adsorption isobars of hydrogen was also observed by us [19-24]. In the present paper we make an attempt to present a new explanation of the nature of the maximum in the adsorption isobars, based on the coordination of the existing material, our own experimental data and the previously published thermochemical calculations, as well as the thermodynamic calculation made jointly with Vol'kenshtein and presented with his permission.

1. The appearance of the maximum in the adsorption isobars is usually explained according to Taylor [8, 9]; it is presupposed that the region of the adsorption isobar between −195° and −78° does not correspond to an adsorptional equilibrium and it is asserted that the rise in summary adsorption and the attainment of the maximum by it at −78° to 0° is caused by the gradual increase of filling of the surface owing to the play of the kinetic factors connected with the transition of the physically adsorbed hydrogen into the activated adsorbed state. However, under this interpretation a series of facts which are incompatible to it and some well founded concepts are ignored.

It is known that the van der Waals adsorption of substances is measurable only below their critical temperature; considering that the critical temperature of hydrogen is equal to −239°, one can assert that at −195° and above, and especially at such low pressures as 10^{-3} to 10^{-1} mm of mercury, the physical adsorption of hydrogen should be negligibly small. Some data on adsorption of hydrogen at −195° to −183° on glass or on clean surfaces of layers of copper, silver, zinc and cadmium [18-21, 27], confirm this concept: the adsorption is extremely small and the filling of the surfaces of these metals with hydrogen at −195° or −183° at pressure of 10^{-2} mm of mercury does not exceed 1%. At the same time the adsorption of hydrogen on nickel, iron, platinum, tungsten and other such metals at −195° is so great that it is sufficient to fill their surfaces by 50% in the case of molecular state or by 100% if the adsorbed hydrogen is in the atomic state. This fact raises doubts about the van der Waals character of the adsorption. If at the same time one considers that almost the entire amount of hydrogen (~ 98%) adsorbed at −195° is bound firmly and is not removed by many hours of pumping at 10^{-7} mm of mercury, and that at above 10^{-3} mm of mercury the adsorption is practically constant and does not depend on pressure, the concept of the physical character of hydrogen adsorption must be rejected.

Let us consider the proposition about the increase of filling of the surface of the metals by hydrogen with increase of temperature. This proposition contradicts the data supplied by Beeck and co-workers [10, 12], Rideal and Trapnell [18] and by us [19-24] from the study of adsorption of hydrogen on condensed metal layers. It was established that hydrogen is extremely rapidly chemosorbed at −195° on layers of nickel, iron, chromium, tungsten, and platinum (according to our data over 90% of the total summary magnitude of adsorption takes place in the first minute and the process stops after 15-20 minutes) and that the amount of absorbed gas is sufficient for 100% filling of the surface of these metals by an atomic layer, i.e., surface hydride. According to these studies, oxygen, carbon monoxide and ethylene are chemosorbed just as rapidly on the surface of nickel, iron, chromium, tungsten

and platinum at −195° and their adsorption is sufficient for a complete coverage of the surfaces of the metals. Westrik and Zwitering [28] used this circumstance successfully in the study of iron isomorphism. Thus, the fact of practically complete coverage of the surface of nickel, iron, chromium, tungsten and platinum metals by chemosorbed hydrogen at −195°, as well as by other gases, cannot be doubted and thus excludes the above proposition.

Let us consider the supposition about the nonequilibrium character of the increased hydrogen adsorption with elevation of temperature from −195° to 0°. This supposition is automatically excluded by the above-cited facts and concepts; rapid (according to Beeck − instantaneous) chemosorption of hydrogen at −195° and the complete coverage of the metal surfaces by a layer of a surface hydride. In addition one should consider that even in the work of Benton and White [1], cited by Taylor [8, 9], in his interpretation of the origin of the maximum of the isobars, the adsorptional equilibrium was attained by either lowering of the higher pressures or by raising the lower ones, at a constant temperature of a run. Frankenbury [7] and Kwan [15-17] checked and verified the equilibrium nature of adsorption on metal powders: the adsorptional equilibrium was reached in their experiments by raising and lowering of temperatures from high to low ones (−78°), i.e., from the direction of adsorption and desorption. It also follows from these data that the rise of the adsorption isobars has an equilibrium character.

It follows from the above that it is impossible to explain the rise of hydrogen adsorption on nickel, iron, platinum and tungsten and the nature of the maximum in adsorption isobars by starting with Taylor's concepts.

Beeck [10, 12] suggested another explanation of the rise of hydrogen adsorption on these metals with the rise in temperature. He found that at even −195° hydrogen is instantly chemosorbed on nickel, iron, chromium and platinum and covers their surface to 100% by an atomic layer. The layer of the surface hydride (provisionally Me^{+}-H^{-}) remains unchanged on being heated to −78° or 0°. A decomposition of the surface hydride sets in at above 0° and the fraction of the surface occupied by atomic hydrogen decreases. Beeck concluded, on the basis of these data, that the reversible sorption of hydrogen is a dissolution and that the sole reason for the increase of hydrogen absorption is the rise of its solubility in nickel, iron, tungsten and platinum, as well as similar metals, with a rise in temperature.

Some of the positions of Beeck's argument were confirmed by the later workers: the practically complete coverage of the surface of nickel and similar metals by atomic hydrogen at −195° was confirmed by the work of Rideal [18], Trapnell [19] and our own work [19-24]. It is also known that the solubility of hydrogen in these metals rises with the rise in temperature although on the whole it is not large. Conversely, the other suppositions made by Beeck were not confirmed: studies made by Rideal, Trapnell and us, as well as Mignolett [26], established the fact that hydrogen firmly adsorbed at −195° is already partly desorbed at this temperature as well as at −183° and −78° while the atomic coverage on the surface decreases regularly with rise in temperature, and that the reversible adsorption of hydrogen is not a dissolution (it is observed already at −195°, when the processes of diffusion are severely restricted, and occurs instantly). Beeck's interpretation also does not agree with the character of the adsorption isobars measured by raising and lowering the temperature [12, 23, 32]: if the increase of adsorption during the rise in temperature from −195° to 0° may qualitatively follow Beeck's explanation, the additional absorption upon the reverse lowering of the temperature from 0° to −195° is completely incompatible with it. Beeck [12] attempted to eliminate these difficulties by supposing that the atomic adsorption is complicated during the elevation in temperature by some other exothermic processes: dissolution, adsorption and, possibly, hydride formation. These suppositions, however, have no basis: the solution of hydrogen in nickel, iron, chromium and platinum increases with elevation in temperature and is an endothermic process; no hydrides are formed thereby and, finally, considering Beeck's [10] assertion about the 100% coverage of the surface of these metals by atomic hydrogen from −195° to 0-20°, one should exclude any additional adsorption: it could be possible through physical adsorption over and above the atomic and chemosorbed hydrogen and could be noticeable at near critical temperature of hydrogen (−239.9°) and below −195°. Evidently, the idea of the atomic adsorption of hydrogen at all temperatures above −195° is not sufficient to explain the existing experimental data.

2. Starting with the peculiarities of the reversible adsorption of hydrogen on nickel, iron, chromium and platinum, we supposed [19-25] that it was molecular chemosorption, while we concluded, on the basis of literature material [29, 30] that a molecule of chemosorbed hydrogen is a positive end of the dipole $Me-H_2$ (provisionally Me^{-}-H_2^{+}). Other workers have now come to the same conclusion [26, 31]. The concepts of the atomic state of irreversibly adsorbed hydrogen and the molecular state of reversibly adsorbed hydrogen allow one to explain successively both our and the other literature data on the adsorption of hydrogen on nickel, iron, chromium and tungsten, as well as similar metals; adsorption of hydrogen proceeds extremely rapidly at −195° and is accompanied

by the dissociation of its molecules into atoms. However, at even this temperature there takes place a recombination of the chemosorbed hydrogen atoms, and a reversible equilibrium chemosorption of hydrogen molecules occurs on the part of the metal surface which is free of the atomic chemosorbed hydrogen. The recombination of hydrogen atoms increases with the elevation of temperature and the part of the metal surface, free of the surface hydride, increases. This leads to the enhanced reversible molecular chemosorption of hydrogen molecules since on each vacant surface atom of the metal an entire molecule of hydrogen may adsorb in place of one hydrogen atom, i.e., two atoms of gas would take the place of one. The combination of atomic and molecular chemosorptions of hydrogen and the increase of the fraction of the latter with the rise in temperature, is the reason for the increase of the summary adsorption. This means that for adsorption of hydrogen at all temperatures the following condition must be fulfilled:

$$2N_a + N_{m\,max} = n_0 = \text{const}, \tag{1}$$

where n_0 is the number of surface atoms of the metal; N_a is the number of irreversibly adsorbed molecules; $N_{m\,max}$ is the maximum possible number of reversibly adsorbed molecules. The adsorption of hydrogen, in this light, is composed of the following stages:

$$H_{2(gas)} \rightleftarrows H^{(+)}_{2ads} \rightleftarrows 2H^{(-)}_{ads} \tag{2}$$

Relation (1) may be observed strictly only in an ideal case; in reality, the sum of $2N_a + N_{m\,max}$ should increase owing to the effect of dissolution with elevation of temperature (the magnitude of N_a would rise). During a drop in the temperature the curve of the summary adsorption should drop also, but owing to the effect of dissolution in the layer and the evaporator it would not coincide with the curve obtained during the rise of temperature. Owing to the dependence of the reversible molecular chemosorption on pressure, the curve of summary absorption at a given pressure may at first rise during a lowering of the temperature, then fall, after passing a maximum at some temperature.

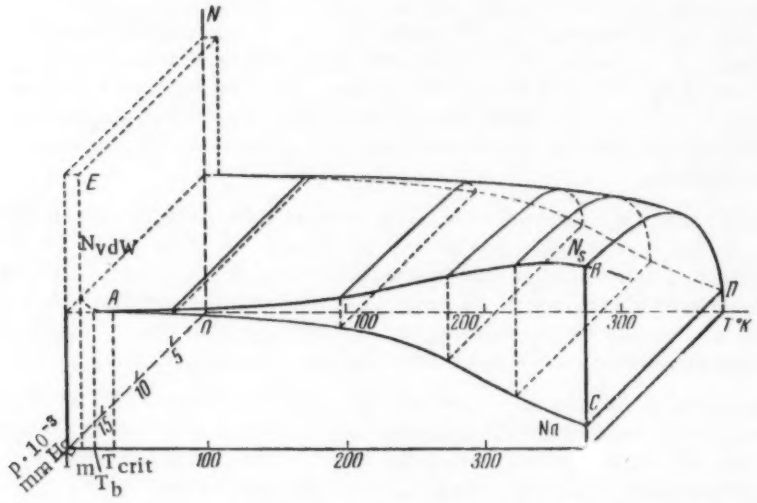

Fig. 1. A scheme of adsorption of hydrogen on nickel: AB) summary adsorption ($N_s = N_a + N_m$); AC) atomic adsorption (N_a); BD) isotherm of reversible molecular chemosorption (N_m); AE) van der Waals adsorption (N_{vdW}); T_m) melting point of hydrogen (−262°); T_b) boiling point of hydrogen (−252.8°); T_{crit}) critical temperature of hydrogen (−239.9°).

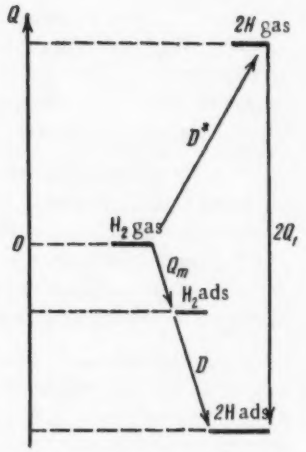

Fig. 2. Scheme of the adsorption of hydrogen on nickel, iron, chrome, platinum and other metals.

The explanation of hydrogen adsorption on nickel, iron, chromium and platinum, based on the equilibrium coexistence of atomically and molecularly chemosorbed hydrogen, is clearly illustrated by the scheme of hydrogen adsorption on nickel [24, 32] (Fig. 1). It follows from this scheme that at very low pressures the adsorption isobars fall with the rise in temperature; at higher pressures they at first rise, then fall after passing through a

maximum at some value of T, with the gradual rise in temperature. The location of the maximum in the adsorption isobars is displaced with increased pressure in the direction of higher temperatures, while the magnitude of adsorption, which corresponds to the maximum, increases. The adsorption of hydrogen on iron, chromium, platinum and similar metals may be represented by similar tridimensional diagrams.

Let us consider the possibility of a mutual transition of atomic and molecular chemosorption of hydrogen by a thermodynamic calculation according to Hess's law. Let us determine the heat effect of the surface reaction $2Me-H + H_2(gas) \rightleftharpoons 2MeH_2$, from the following equations:

$$Me + H_2\,gas \rightleftarrows MeH_2 + Q_m; \tag{3}$$

$$2Me + H_2\,gas \rightleftarrows 2MeH + Q_a. \tag{4}$$

It follows from Formulas (3) and (4) that:

$$Me + Me - H_2 \rightleftarrows 2MeH + D, \tag{5}$$

where $D = Q_a - Q_m$ and

$$2Me - H + H_2\,gas \rightleftarrows 2Me - H_2 - (Q_a - 2Q_m). \tag{6}$$

The heat effect of process (6) depends on the ratio of Q_a and Q_m: if Q_a is smaller than $2Q_m$, the transition of atomic chemosorption into molecular chemosorption is an endothermic process; while if Q_a is greater than $2Q_m$, it is an exothermic process. The initial values of the differential heats of atomic adsorption are 60 — 40 kilocalories per mole, according to our [25] and literature data [12], while those for the molecular chemosorption are 9-4 kilocalories per mole by our calculations and about 8 kilocalories per mole from Mignolett's data [26] on tungsten. Therefore, in the beginning of adsorption Q_a is greater than $2Q_m$ and the surface is filled only through atomic chemosorption; in the course of the progress of adsorption the differential heat Q_a decreases rapidly and at some value of Θ_a, which corresponds to the given temperature T, the magnitude of Q_a may become equal to $2Q_m$, i.e., $Q_a - 2Q_m = 0$. On further decrease of Q_a, with the filling of the surface, process (6) becomes endothermic. In this case the nature of the dependence: $Q_{ads} = f(\theta)$ should change. This instance, which had been established by us [19-25, 32], corresponds to the sharp change in the differential heats of adsorption during the transition from atomic adsorption to molecular chemosorption.

At T' being greater than T, the transition from atomic adsorption to molecular chemosorption occurs at Θ_a' being smaller than Θ_a. This corresponds to an endothermic character of the transition of the atomic adsorption to the molecular chemosorption at filling Θ_a'' that is smaller than Θ_a' and indicates the displacement of reaction (6) in the direction of molecular chemosorption.* An increase of the fraction of molecular chemosorption of hydrogen with increased temperature causes the increase of its summary adsorption at "high" pressures. Reaction (6) is displaced to the left with decline in the temperature, which fact leads to a drop in summary adsorption.

3. The thermochemical foundation of the increase of the summary adsorption on elevation of temperature, as well as the explanation of the nature of the maximum in the adsorption isobars, may be augmented by a thermodynamic calculation. It is possible that this calculation will characterize some peculiarities of hydrogen chemosorption on nickel, iron, chromium and platinum, previously established by us, in a more evident manner. According to the mechanism of hydrogen chemosorption proposed by us (2) and shown schematically in Fig. 2, let us assume that n_0 is the number of surface atoms of the metal; N_1 is the number of chemosorbed atoms of hydrogen (i.e., $N_1 = N_a/2$); N_2 is the number of chemosorbed molecules of hydrogen (i.e., $N_2 = N_m$); n is the number of free surface atoms of the metal. Then the total number of centers on the surface n_0 and the total quantity of adsorbed gas N_s, expressed in the number of atoms, would be equal to each other:

$$n_0 = n + N_1 + N_2. \tag{7}$$

* Values Θ_a, Θ_a' and Θ_a'' indicate the fraction of coverage of the surface by atomic hydrogen at $T < T' < T''$.

$$N_s = N_1 + 2N_2. \tag{8}$$

If we suppose for simplicity of calculation that the heats of adsorption are independent of the degree of filling and of the temperature, and if we neglect the desorption of the chemosorbed atoms into the free state in surrounding space, bypassing the molecular form, then we have for the whole process in toto, using Equations (3) and (5) for each of the stages of hydrogen chemosorption;

$$Q_m + D - 2Q_A + D^* = 0 \quad \text{or} \quad Q_A = \frac{1}{2}(Q_m + D + D^*), \tag{9}$$

where Q_A is the heat of adsorption of free hydrogen atom with formation of Me−H; Q_m is the heat of adsorption of a molecule of hydrogen with formation of Me−H_2; D is the heat evolved during the transition of molecular form of chemosorption into the atomic form [$D = Q_a - Q_m$]; D^* is the dissociation energy of a free molecule H_2 into two free hydrogen atoms (Fig. 2). The conditions of equilibrium may be written for both stages of hydrogen chemosorption (3) and (5).

I. For the stage $Me + H_2 \rightleftharpoons MeH_2$:

$pn = aN_2$, where $a = k_1 \exp[-Q_m/RT]$ and p is hydrogen pressure,

$$\text{i.e.,} \quad \frac{pn}{N_2} = k_1 \cdot e^{-Q_m/RT} \tag{10}$$

II. For the stage $- MeH_2 + Me \rightleftharpoons 2MeH$:

$N_2 n = bN_1^2$ where $b = k_2 \exp[-D/RT]$

$$\text{i.e.,} \quad \frac{N_2 n}{N_1^2} = k_2 e^{-D/RT} \tag{11}$$

It follows from Equations (10) and (11) that:

$$N_1 = n \sqrt{\frac{p}{k_1 k_2}} \cdot e^{\frac{D + Q_m}{2RT}} \tag{12}$$

and

$$N_2 = n \cdot \frac{p}{k_1} \cdot e^{\frac{Q_m}{RT}} \tag{13}$$

or by substituting Equations (12) and (13) into (7):

$$N_1 = n_0 - N_2 \left(1 + \frac{k_1}{p} \cdot e^{-\frac{Q_m}{RT}}\right). \tag{14}$$

$$N_2 = n_0 - N_1 \left(1 + \sqrt{\frac{k_1 k_2}{p}} \cdot e^{-\frac{D + Q_m}{2RT}}\right). \tag{15}$$

By substitution of Equations (15) into (14) and (14) into (15) we have:

$$N_1 = \frac{n_0}{1 + \sqrt{\frac{k_1 k_2}{p}} \cdot e^{-\frac{D + Q_m}{2RT}} \left(1 + \frac{p}{k_1} \cdot e^{\frac{Q_m}{RT}}\right)} \tag{16}$$

and

$$N_2 = \frac{n_0}{1 + \frac{k_1}{p} \cdot e^{-\frac{Q_m}{RT}} \left(1 + \sqrt{\frac{p}{k_1 k_2}} \cdot e^{\frac{D+Q_m}{2RT}}\right)}. \tag{17}$$

Let us consider the effect of the conditions, i.e., temperature and pressure on the magnitude of the atomic and the molecular chemosorption of hydrogen, on their relative proportions and on the magnitude of the summary adsorption, assuming that the heat of molecular chemosorption Q_m is smaller than the heat $D (D > Q_m)$.

1. In the region of "low" pressures,* i.e., when

$$\frac{p}{k_1} \cdot e^{Q_m/RT} \ll 1 \text{ and } \sqrt{\frac{p}{k_1 k_2}} \cdot e^{\frac{D+Q_m}{2RT}} \ll 1. \tag{18}$$

Relations (16) and (17) have the form:

$$\frac{N_1}{n_0} = \sqrt{\frac{p}{k_1 k_2}} \cdot e^{\frac{D+Q_m}{2RT}}; \tag{19}$$

$$\frac{N_2}{n_0} = \frac{p}{k_1} \cdot e^{Q_m/RT}. \tag{20}$$

It follows from Equations (19) and (20) that at p = constant, the amount of atomically (N_1) and molecularly (N_2) chemosorbed hydrogen decreases with elevation of temperature.

We have from Formulas (19) and (20) that:

$$\frac{N_2}{N_1} = \sqrt{\frac{k_2}{k_1}} \cdot p \cdot e^{-\frac{D-Q_m}{2RT}}. \tag{21}$$

according to Equation (21) at p = constant, the relative content of the molecularly chemosorbed hydrogen rises with elevation of temperature; at T = constant, the relative amount of molecularly chemosorbed hydrogen rises also with increased pressure. It follows from Equation (21) that almost all the chemosorbed hydrogen can be found in the atomic state $(N_2/N_1) \ll 1$, when $p \ll (k_1/k_2) \cdot \exp[(D - Q_m)/2RT]$ at "low" pressures or "low" temperatures.

And, finally, let us determine the dependence of the summary adsorption of hydrogen on the conditions of p and T in the region of "low" pressures. For doing this, let us substitute Equations (19) and (20) into (8) and obtain:

$$N_s = n_0 \sqrt{\frac{p}{k_1}} \cdot e^{Q_m/2RT} \left(2 \sqrt{\frac{p}{k_1}} \cdot e^{Q_m/2RT} + \frac{1}{\sqrt{k_2}} \cdot e^{D/2RT}\right). \tag{22}$$

It follows from Equation (22) that at T = constant, the summary hydrogen adsorption rises with increased pressure and that at p = constant it falls with elevation of temperature.

2. In the region of "high" pressures,** i.e., when:

$$\frac{p}{k_1} \cdot e^{Q_m/RT} \gg 1 \text{ and } \sqrt{\frac{p}{k_1 k_2}} \cdot e^{\frac{D+Q_m}{2RT}} \gg 1, \tag{23}$$

* Or "low" temperatures.
** Or "high" temperatures.

the Relations (16) and (17) assume the following form:

$$\frac{N_1}{n_0} = \frac{1}{1 + \sqrt{\frac{k_2}{k_1}} p \cdot e^{-\frac{D-Q_m}{2RT}}}; \tag{24}$$

$$\frac{N_2}{n_0} = \frac{1}{1 + \sqrt{\frac{k_2}{k_1}} \cdot \frac{1}{\sqrt{p}} \cdot e^{\frac{D-Q_m}{RT}}}. \tag{25}$$

It follows from Equations (24) and (25) that at p = constant, the amount of atomically chemosorbed hydrogen declines with elevation of temperature while the amount of molecularly chemosorbed hydrogen rises under this condition; at T = constant, and the amount of atomically chemosorbed gas falls with rising pressure, while the amount of molecularly chemosorbed hydrogen increases thereupon.

From Equations (24) and (25) we have:

$$\frac{N_2}{N_1} = \sqrt{\frac{k_2}{k_1}} \cdot p \cdot e^{-\frac{D-Q_m}{2RT}}. \tag{26}$$

According to Equation (26) at p = constant the relative content of the molecularly chemosorbed hydrogen rises with elevation of temperature; at T = constant it also increases with increased pressure as in the region of "low" pressures.

In conclusion, let us determine the dependence of the summary adsorption of hydrogen on the conditions of the region of "high" pressures as well. For this, let us substitute Equations (24) and (25) into (8) and obtain:

$$\frac{N_s}{n_0} = 1 + \frac{1}{1 + \sqrt{\frac{k_1}{k_2}} \cdot \frac{1}{\sqrt{p}} e^{\frac{D-Q_m}{2RT}}}. \tag{27}$$

It follows from Equation (27) that at T = constant, the summary adsorption of hydrogen rises with increased pressure while at p = constant it rises also with elevation of the temperature. At T = constant ($T \neq 0$) and $p \rightarrow \infty$, the ratio $(N_s/n_0) \rightarrow 2$; conversely, at p = constant and $T \rightarrow 0$, the ratio $(N_s/n_0) \rightarrow 1$. It follows from this that the summary adsorption at high temperatures may exceed the summary adsorption at low temperatures by approximately two-fold. According to Equations (22) and (27), the character of the change of the summary adsorption, depending on the elevation of temperature at constant pressure, i.e., the course of the adsorption isobars, differs in various regions of pressure: at "low" pressures the summary adsorption decreases with elevation of temperature, while at "high" pressures it increases. It follows from this that in the region of "medium" pressures a maximum exists in the adsorption isobars.

The results of the calculation of chemosorption of hydrogen on nickel, iron, chromium, tungsten, platinum and similar metals agree completely with the experimental data and conclusions made by us in previous work. The real picture of chemosorption is, of course, more complicated than that which follows from the thermodynamic examination given above; hence, for a more complete representation of this picture it will probably be necessary in future calculations to include first of all the dependence of the heats of adsorption on the degree of filling of the metal surface by both forms of chemosorbed hydrogen.

The problem of chemosorption of hydrogen is evidently a special case of the general problem of chemical adsorption of gases on metals. Therefore, the various effects and regularities of hydrogen chemosorption, which were established experimentally and which followed from even the simplified theoretical calculation, could also be found in the study of adsorption of other diatomic and possibly triatomic, and higher, gases on metal surfaces. This conclusion is based on a number of experimental facts established by us previously [19-25, 32], as well as by other workers [31, 33], as well as from certain theoretical concepts, specifically in the Frank-Condon principle [34-38]. A detailed discussion of this problem may be the subject of another paper.

In conclusion the author expresses his gratitude to F. F. Vol'kenshtein for his aid in the thermodynamic calculation and for the constant interest in this work.

SUMMARY

1. The existing explanations of the nature of the maximum in the isobars of adsorption of hydrogen on nickel, platinum, iron, chromium and similar metals were examined.

2. A new explanation was proposed for the nature of the maximum in the adsorption isobars, based on the concept of an equilibrium coexistence of atomic and molecular chemosorption of hydrogen on nickel, iron, chromium, platinum and similar metals.

3. A thermochemical and thermodynamic foundation was supplied for the proposed explanation.

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PROPERTIES AND STRUCTURE OF $NiO-Al_2O_3$ CATALYSTS

3. A STUDY OF THE RELATION BETWEEN COMPOSITION, MAGNETIC PROPERTIES AND ACTIVITY

A. M. Rubinshtein and A. A. Slinkin

We described in paper [1] some $NiO-Al_2O_3$ catalysts and the results of determination of their activity and selectivity of action in the decomposition of isopropyl alcohol depending on the composition and conditions of thermal treatment. Paper [2] was devoted to the x-ray study of these catalysts in which we established their phase composition and considered the relations between the structural and the catalytic properties. In the present work, which was done simultaneously with the studies described in [1, 2], we present the results of a study of the magnetic properties of the same $NiO-Al_2O_3$ catalysts.

Only two papers exist in the literature on the magnetic properties of the system $NiO-Al_2O_3$. Thus, Hill and Selwood [3] studied the magnetic properties of $NiO-Al_2O_3$ catalysts, containing up to 24% Ni, which were prepared in deposited form by saturation of γ-Al_2O_3 by a solution of nickel nitrate and heating (450°); they determined the activity of these catalysts only after the reduction. The main conclusions from this work are contained in the following: the Curie law is obeyed by only a part of the system in the region of weight concentrations of nickel up to 6%, while the Weiss constant is close to zero; hence, Hill and Selwood consider that this constant fails to provide any information about the structure of NiO in the samples studied by them. Furthermore, from the alteration of the magnetic moment from 3.2 Bohr magnetons at 2% Ni to 2.6 magnetons at 6% Ni, the authors deduced the "valence inductivity," i.e., alteration of the valence state of nickel at its low concentration under the influence of the support, and proved the presence of Ni^{3+} by the number of equivalents of hydrogen consumed in the reduction of the nickel to the metal. The catalytic activity in reactions of benzene hydrogenation was determined at 125° by these authors over catalysts which had been reduced at 510° over 16 hours. The observation by these authors that the maximum activity of these supported catalysts is reached at 8% Ni on aluminum oxide is quite interesting. It should be added that Hill and Selwood proved, by alternate reduction and oxidation and by measurement of the magnetic susceptibility, that the reduction of NiO in this system does not bring about any substantially irreversible changes in its structure.

Milligan and Richardson [4] studied coprecipitated specimens of $NiO-Al_2O_3$ without a determination of their catalytic reactivity. They found, for specimens heated to 300°, some sharp minima and maxima in the curve of susceptibility-composition in the region of 60-100 mole % NiO, which disappeared at higher temperatures of heating. The authors explain these minima and maxima by "mutual protection" of the components from crystallization, while their disappearance is explained by sintering. Milligan and Richardson found that the magnetic moment changes with NiO concentration but within somewhat different limits than in case of paper [3] – from 3.2 to 2.7 Bohr magnetons respectively at 2 and 15 weight % NiO. It should be noted that the distributions of NiO in the coprecipitated and deposited specimens of $NiO-Al_2O_3$ are substantially different and, hence, the analogy given in paper [4] in respect to paper [6] is hardly valid.

These data exhaust the literature sources about the magnetic properties of the $NiO-Al_2O_3$ system, although there is a study of the magnetic properties of pure NiO [5], in which the changes of magnetic susceptibility of the samples with variation of temperature of heating are explained by antiferromagnetic properties of NiO and by their disruption as a result of surface oxidation (O_2, H_2O), as well as by alteration of the number of "magnetic neighbors," i.e., nickel ions which surround a given nickel ion.

As is evident from the above, no direct determinations of the relationship between magnetic and catalytic properties of the $NiO-Al_2O_3$ system had been made and no correlation with the x-ray structural data for this system had been made either. Nevertheless, from the viewpoint of catalysis, the clarification of the degree of correlation of properties determinable by different methods is quite interesting. This was the aim of the present work along with a detailed characterization of the alteration of the magnetic properties in $NiO-Al_2O_3$ system, obtained under definite conditions in the medium and of the thermal treatment. The clarification of such correlation was of even greater interest since in paper [2] we showed the effect of NiO content on the phase composition of the $NiO-Al_2O_3$ catalysts subjected to thermal treatment at 400° and higher, which were generally not discussed in papers [3, 4]. We determined the magnetic susceptibility χ, its change with temperature, the magnetic moments μ and the Weiss constants Δ.

EXPERIMENTAL

Catalysts with the content of 0, 4, 9, 14, 20, 31, 51 and 59 mole % NiO were prepared [1] by precipitation of mixtures of the hydroxides from mixtures of 10% solutions of nickel and aluminum nitrates by means of 10% ammonium hydroxide. The thermal treatment of the precipitates, which had been washed and dried at 110° was run for 7 hours at 400, 600 and 750°. In the following material these catalysts are indicated as to the NiO content with an index showing the heating temperature (for example 31_{750}, 9_{600} etc).

The apparatus for the measurement of the magnetic susceptibility consisted of an electromagnet described by Wedekind [6] but a stronger one (H to 12,000 oersteds), equipment for the measurement and regulation of current strength and a microbalance M-20 with optical indicator, the balance having been remodeled to the antimagnetic form, with sensitivity of $1.1 \cdot 10^{-5}$ g (one scale division equal to 0.011 mg). The calibration of the apparatus was done with $NiCl_2$ solutions, with Ni concentrations of 12.95 and 18.06%, checked by analysis. The susceptibility of these solutions, calculated by formula from [7], $10^6\chi = 10{,}030\,a/T - 0.720\,(1-a)$, (where a – weight % of $NiCl_2$) was $\chi_{12.95} = 3.971 \cdot 10^{-6}$ and $\chi_{18.06} = 5.634 \cdot 10^{-6}$. The solutions for calibration, and in the fundamental experiments – samples of the catalysts – were placed into thin (cross section 0.071 or 0.076 cm^2) test tubes with a ground-in stopper and with hooks for suspension. Corrections for the weight change of these test tubes in the magnetic field were always used and these were determined directly in terms of scale divisions of the microbalance for each current strength. For experiments at elevated temperatures we also determined the corrections for the weight of the test tubes which were dependent on the temperature.

Measurements of χ of the catalysts, except for 0_{400} and 0_{750} – pure Al_2O_3, studied by the method of Gouy, were run at field strengths of 1000-5000 oersteds by the Faraday method with Sacksmith terminations having a diameter of 50 mm. The distance between the pole-pieces was 16.65 mm in experiments at 20°, while in experiments at elevated temperatures this was 29.00 mm, owing to the necessity of introduction of the heater into the interpolar space. Therefore, the equipment calibration was done twice for both interpolar distances, while the maximum value of $H \cdot dH/dx$ was determined prior to the calibration. In later experiments the test tube was always kept at this height. The heater was a quartz test tube with two connections for thermocouples from below and at the middle of the specimen, these connections being made with bifilar winding covered with a double layer of an asbestos cord. The pole terminations were not heated at the measurement temperatures.

All catalysts samples were heated for one hour at 400°, prior to the measurements, for removal of moisture which could have been adsorbed in storage. The measurements were made on specimens which had been ground in an agate mortar to a uniform powder. The samples varied within the limits of 0.01-0.03 g. The reproducibility of each measurement was checked.

The measurements made on all the catalysts at various field strengths showed that they do not contain any ferromagnetic impurities. The susceptibility of Al_2O_3, determined by Guoy method, was found to be $0.38 \cdot 10^6$. Measurements of the susceptibility of the catalysts were made at 20°, 80° and 160° and the resulting values ($\chi \cdot 10^6$) related to 1 g of the sample are given in the table. The values of susceptibility per 1 g of nickel, χ_{Ni}, were calculated from the data shown in this table and these are given on Fig. 1 along with the values of χ.

Values of χ_{Ni} were used for the determination of the magnetic moments μ of the catalysts studied by us, using the formula $\mu = 2.84\sqrt{C}$, where C – Curie constant, from the slope of the straight lines constructed for each series of the catalysts (400, 600 and 750°) in the coordinate system $T°K - (1/\chi_{Ni}) \cdot 10^4$ which are not shown on the graphs of this publication for the reasons of economy of space. The values of Weiss constant were

also calculated from the values of C. The magnetic moments were determined with an accuracy of ±0.1 μ_B (Bohr magneton), while Δ were determined with accuracy of ±15.

Discussion of Experimental Results

Before making a comparison of the magnetic properties with the structure derived from x-ray studies and with the activity of the catalysts studied by us, let us consider the character of the change of the magnetic properties themselves depending on the composition and the conditions of the thermal treatment of the catalysts.

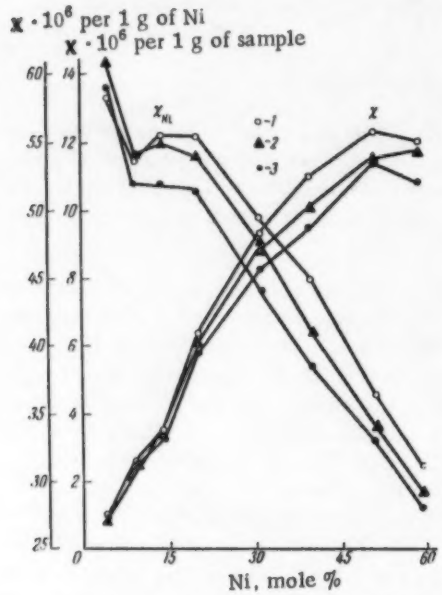

Fig. 1. Susceptibility of the catalysts (χ) and susceptibility per 1 g of nickel (χ_{Ni}) at the heat treatment temperature: 1) 750°; 2) 600°; 3) 400°.

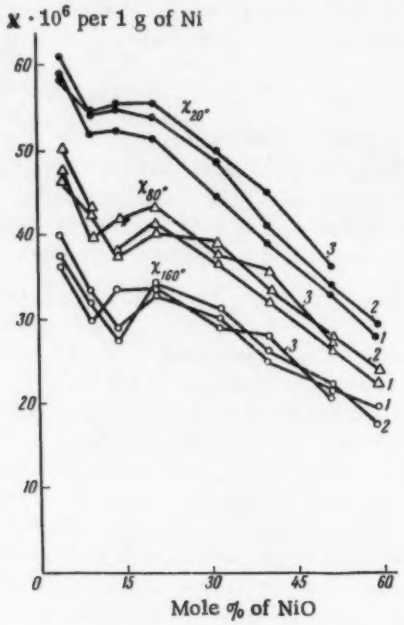

Fig. 2. Dependence of χ on the temperature for catalysts heat treated at 400°, 600° and 750°: 1) 400°, 2) 600°, 3) 750°.

TABLE 1

Magnetic Susceptibility per 1 g of Catalyst : $\chi \cdot 10^6$

Heat treatment temp., °C	400			600			750		
NiO content in mole %	Measurement made at			Measurement made at			Measurement made at		
	20°	80°	160°	20°	80°	160°	20°	80°	160°
4	0,98	0,75	0,50	1,02	0,70	0,48	0,97	0,70	0,47
9	2,5	2,0	1,5	2,6	2,0	1,4	2,6	1,8	1,3
14	3,3	2,3	1,7	3,3	2,3	1,6	3,4	2,6	2,0
20	5,8	4,6	3,6	6,1	4,8	3,7	6,3	4,8	3,4
31	8,3	6,8	5,4	8,9	7,3	5,8	9,3	7,0	5,2
40	9,5	7,8	6,1	9,8	8,0	6,4	11,0	8,8	6,8
51	11,4	9,0	7,2	11,7	9,3	7,4	12,3	9,3	7,2
59	11,0	8,8	6,6	11,4	8,9	6,7	—	—	—

It is clear from Fig. 1 that the magnetic susceptibility, calculated per 1 g of the catalysts, χ, rises steadily until reaching the NiO concentration of 51 mole %, while the temperature of the heat treatment of the catalysts manifests itself in the value of χ to a noticeable degree beginning, approximately, with 30 mole % of NiO. Increased NiO content up to 59 mole% for cases of 59_{400} and 59_{750} leads to a small decrease of χ which does not change

in case of 59_{600}. The susceptibility calculated per 1 g of Ni, however, decreases with increased content of NiO, while in the region of about 10 mole % NiO in the catalyst there exists a clear minimum and, beginning at about 20 mole % NiO the decrease of χ_{Ni} proceeds smoothly. The same picture appears under all conditions of heat treatment of the catalysts – the curves of change of χ_{Ni} vs. the composition, for 400°, 600° and 750° were in general symbatic and had a minimum in the same region. This minimum deepened with elevation of the temperature of measurement of the magnetic susceptibility as is evident from Fig. 2, where we show the values of χ_{Ni} measured at 20°, 80° and 160°. Thus, it is possible to state that an extremal region exists in the change of χ_{Ni} with catalyst composition.

Construction of graphs, based on the values of χ_{Ni} and the coordinate system of $T_{abs} - 1/\chi_{Ni}$, and the calculation of constant C led to a rather important result: it appeared that the $NiO-Al_2O_3$ system, coprecipitated under the conditions indicated above over the entire interval of NiO concentrations up to 59 mole % at which NiO is already in excess relative to Al_2O_3, obeys the Curie law with positive values of the Weiss constant Δ. It should be noted that in paper [3] only those of the supported catalysts obeyed the Curie law in which the Ni concentration did not exceed 6 weight %, which was also taken, without a check, to be true in work [4] done with coprecipitated catalysts. As is evident from the above, in reality a great difference was discovered in the obedience to the Curie law by the coprecipitated and the deposited catalysts.

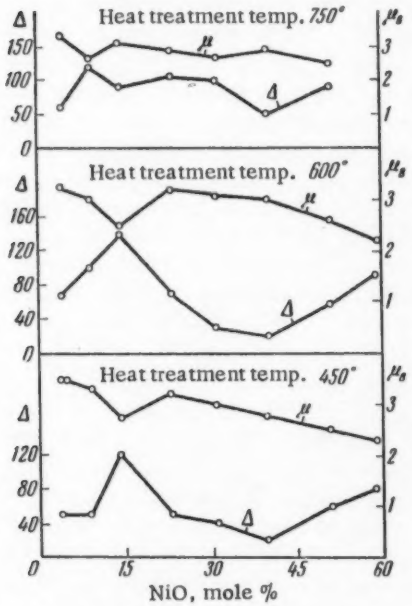

Fig. 3. Dependence of the magnetic moment (μ) and Weiss constant (Δ) on the composition of catalysts heat treated at 400°, 600° and 750°.

The changes in the magnetic moments μ (in Bohr magnetons) and the constant Δ with the composition of the catalysts for all three temperatures of their heat treatment are given in Fig. 3. First of all Fig. 3 shows that at 400° and 600° the path of the changes in μ and Δ with composition is similar, while at 750° there is observed a more complex path of these curves. Nevertheless the main regularity, which is common for all three temperatures, lies in:

1) μ declines from 3.2 μ_B to a minimum of about 2.5 μ_B in the region of 10-15 mole % NiO, then rises, with increasing concentration of NiO to about 30 mole %, to about 3.0 μ_B, and again declines, although more slowly, upon further increase of NiO concentration.

2) The path of the Weiss constant Δ has a sharp maximum in the region of 10-15 mole % NiO, then declines down to the content of 51 mole % NiO and again rises upon further increase of NiO concentration.

The magnetic moment, which is equal to 3.2 μ_B instead of 2.8 for Ni^{2+}, at the lowest NiO concentration, and its decline with increased NiO concentration, indicate the presence of nickel in a valence state different from divalent, in the catalysts with $\mu > 2.8\ \mu_B$, and the decrease in the concentration of such nickel with increased NiO content in the catalysts. In order to explain the appearance of Ni ions having a valance other than two, it is necessary to consider: a) the antiferromagnetic nature of NiO, i.e., the possibility of formation of ions Ni^+, having 3 unshared electrons and, consequently, causing the increase of μ relative to the values for Ni^{2+}, along with the Ni^{3+} ions, and b) the phenomenon of "valence induction" discovered by Selwood.

Since Ni^{2+} had two unshared d electrons, one of the possibilities under this discussion is the formation of pairs of ions Ni^{3+} and Ni^+ as the result of a direct exchange between two Ni^{2+} ions according to the scheme proposed by Mott [8] for the explanation of the appearance of conductivity in NiO which is an insulator under the usual conditions. This hypothesis in inapplicable for the explanation of the increased μ at certain concentrations of NiO in the catalysts, since: 1) μ is larger at low concentrations of NiO, i.e., when the conditions for Ni^{2+}-Ni^{2+} exchange are hindered or impossible owing to the great distance between them; 2) the energy of formation of such pairs is great; 3) a calculation of the values of μ, made by us from the measurements of χ_{Ni} at the temperatures of 20°, 80° and 160°, showed that the magnitude of the moment decreases in this series, while in the

cases of applicability of this scheme, μ should be rising. Thus, the increase of μ at the expense of a simultaneous formation of Ni^{3+} and Ni^{+} cannot apply in our case.

The second possibility – the appearance of only the Ni^{+} ions as the result of an indirect exchange of Ni^{2+}-Ni^{2+} through ion O^{2-}, which yields one electron to the Ni^{2+} ion by the Heikes' scheme [9], was also suggested for the explanation of conductivity in NiO. The fact that at a low NiO concentration in Al_2O_3 the probability of proximity of two Ni^{2+} ions at distances necessary for such an indirect exchange is small, is in our case against this scheme, which like Mott's scheme is completely applicable to NiO itself. In reality, taking into account the x-ray structural character of the phase, which represents all our catalysts with NiO under 50 mole %, as spinel $NiAl_2O_4$ or its solid solution with γ-Al_2O_3, and calculating the number of Ni atoms per unit cell, it appears that this is equal to 0.5 for 4 mole % NiO, i.e., at the NiO concentration at which μ is maximal or at which not every unit cell of the crystal lattice contains a Ni atom, the indirect exchange by the Heikes' scheme is consequently actually impossible at this NiO concentration; it would have been possible with increase in the NiO concentration but in such a case it is disposed of by the fall of the value of μ with increased content of NiO.

Finally, the third possibility – that of the appearance of Ni^{2+} as the result of valance induction according to Selwood, which represents the alteration of valence under the influence of the support lattice (Al_2O_3 with Al^{3+} ion) – exists. The presence of Ni^{3+} ions was confirmed by Selwood by the number of equivalents of hydrogen needed for the reduction of the supported catalysts. The sole remark, which may be made, is that Ni^{3+} ions could form in the preparation of the supported catalysts by a thermal decomposition of nickel nitrate through its oxidation by nitrogen oxides. However, Selwood's experiments with alternating oxidation and reduction, and the measurement of μ, remove this objection. Thus, valence induction is rather probable in our case as well: the fact that all the conditions for its origination in our catalysts are present speaks in favor of this idea.

Valence induction, which consists of the imitation of the support structure, may appear [10] only under the conditions of: a) isomorphism of the support and the second component of the catalyst; b) diamagnetism of the support; c) proximity of cations in respect to their dimensions. Let us consider whether or not these conditions are fulfilled in the case of the catalysts studied by us. The results of roentgenographic phase analysis [2] acquire a special importance in this case; they showed that catalysts with up to 50 mole % NiO are single-phased and that the change of the lattice parameter with NiO concentration indicates that this phase, a solution of $NiAl_2O_4$ in γ-Al_2O_3, is a solution of isomorphic substances. Consequently, the first condition is satisfied as is the second: γ-Al_2O_3 is diamagnetic. The third condition – equality or closeness of the cation dimensions – is also fulfilled for the Ni^{3+} ion. It is known [11] that the ionic radius of Al^{3+} = 0.57 A, while that of Ni^{2+} = 0.74 A. While direct data about Ni^{3+} are absent at this time, the analogy of Co^{2+} (r = 0.78 A) and Co^{3+} (r = 0.64 A) and Ni^{2+} and Ni^{3+} is quite suitable here, from which it follows that the radius of Ni^{3+} would have the value of the order of 0.6 A.

It is important to note that valence induction, in the case of our coprecipitated catalysts, appeared over a considerable wider range of concentrations (up to NiO of the order of 30 mole %) than in the case of the supported catalysts. This is evidently the result of the fact that in our case there occurred the formation of a spatial spinel structure, while for Hill and Selwood such a structure was possible only as a surface phenomenon from the character of distribution of NiO, this fact being a consequence of the nature of the method of preparation of the catalyst itself. We suppose that specifically this factor caused the appearance of valence induction in their work [5] only in the region of quite low Ni concentrations. Thus it appears completely probable that the cause for the valence induction in the NiO–Al_2O_3 system is the formation of spinel, while the local formation of $NiNi_2O_4$ is not excluded.

The anomalous values of μ indicate, also, that in our catalysts the distances of Ni–Ni were greater than in pure NiO, up to a certain limit of the NiO concentration. The decline of μ with increasing content of NiO is explained naturally by the purely concentrational factor – the effect of the support is weakened by the decrease of its concentration. In addition, the mutual disposition of Ni^{2+}, i.e., its distribution in the catalysts, becomes more and more favorable for an exchange between these ions with increasing NiO content, and for the formation of an intercationic covalent bond through their unshared electrons.

The minimum in the dependence of μ on composition, at 14 mole % NiO, is probably explained by the maximum of mutual interaction of Ni^{2+}-Ni^{3+}, which is indicated by the maximum of the Weiss constant Δ at this concentration. The fall of Δ with a further rise of NiO concentration depends on the fact that with NiO content of up to 50 mole % there exists a solid solution of spinel structure, while the NiO phase is absent, which fact is confirmed by x-ray diffraction. In addition, a decrease in the concentration of Ni^{3+} ions is possible (and consequently, their exchange with Ni^{2+} ions) as is the fact of but a small paramagnetic enclosure of Ni, i.e., Z in the expression $\Delta = -2IZS(S + 1)/3k$ is small. The increase of Δ after 40 mole % of NiO is connected with the beginning of the appearance of the phase of free NiO in these catalysts: the paramagnetic enclosure of Ni in the

crystals of NiO is considerable and the value of Δ increases with the accumulation of this phase. A somewhat different course of changes of μ and Δ is true for the catalysts heat treated at 750° (with preservation of their general character in respect to the catalysts heat treated at 400° and 600°) and this may be explained most readily by the increased order of the spinel structure at the higher temperature.

We suppose that all the above material permits a good correlation of the data from the magnetic measurements and the roentgenographic determination of the phase composition and the structure of the catalysts. As to the relationship between the changes in activity [1] and the magnetic properties, the relationship is indicated by the fact that the maximum of specific activity for the dehydration reaction of iso-C_3H_7OH over the catalysts studied by us falls within the region of 5-15 mole % of NiO, i.e., specifically in the magnetically extreme region whose metastability follows from the sharp alteration of the properties after comparatively small changes of the composition.

SUMMARY

In a magnetic study of the coprecipitated $NiO-Al_2O_3$ catalysts containing up to 59 mole % NiO, which had been subjected to a thermal treatment at 400°, 600° and 750°, the values of χ, μ and Δ were determined, and it was shown that:

1) In contrast to the deposited catalysts [3], the coprecipitated catalysts obey the Curie law over the entire interval of concentrations indicated above, with positive values of the Weiss constant Δ.

2) Valence induction [10], i.e., the formation of Ni^{3+} ions under the influence of the catalyst support, occurs at the NiO concentrations up to 30 mole %.

3) The changes in the magnetic moment and the Weiss constants Δ confirm the formation of spinel $NiAl_2O_4$ and its solid solution with Al_2O_3 in these catalysts.

We established a good correlation of the magnetochemical data with the results of measurement of the activity [1] and of the roentgenographic determination of the structure [2]. It was shown that the extremal region in the graphs of magnetic properties – composition is the optimal one for the dehydrating activity of the catalysts.

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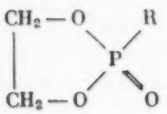
CONCERNING ESTERS OF PROPYLENE HYDROGEN PHOSPHITE AND THEIR TRANSFORMATIONS

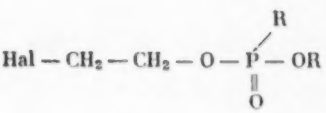
A. E. Arbuzov and N. A. Razumova

The property which most clearly distinguishes the mixed alkylene and arylene cyclic esters of phosphorous acid from the analogous esters with the open chain structure is the difference in their behavior in the rearrangement reaction. It is known that esters with trivalent phosphorus having an open chain structure are transformed into esters of phosphonic acids under the influence of alkyl halides as well as those of other compounds with mobile halogen [1].

Under the same conditions, the cyclic esters of phosphorous acid often behave differently, as it was shown by Arbuzov and Zoroastrova, Rizpolozhenskii and Azanovskaia [2-5]. Some of these esters yield esters of phosphonic acids (substances with unopened rings) under these conditions; for example:



Others yield haloalkyl esters of phosphonic acids (with opened rings); for example:



Thus, the cyclic esters may react dually and such a different behavior has been observed among esters which were very similar to each other in composition. Thus, methyl and benzyl methoxypropylene phosphites are rearranged into the esters of corresponding phosphonic acids with the unopened ring under the action of acetyl bromide, while ethyl, propyl and phenyl esters under the same conditions yield the haloalkyl esters of phosphonic acids with the opened ring [6].

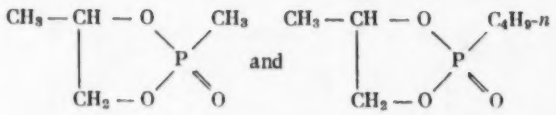
The same picture is observed in the action of benzyl bromide on allyl and benzyl ethylene phosphites. The first of these yields the product with the opened ring, while the other yields one with the unopened ring [7, 8]. It is possible to find similar examples among esters with a five-membered ring in a number of other cases.

The attempts made to explain the different behavior of the cyclic esters in the rearrangement reaction, made by Rizpolozhenskii [6] and Azanovskaia [7], fail to provide a clear and satisfactory answer. Hence, a considerable interest resided in a further study of the rearrangement of such cyclic esters. We synthesized for this purpose, in addition to the esters previously prepared by Lucas and his co-workers [8], a series of previously unknown cyclic esters of propylene hydrogen phosphite which were described in our previous paper [9].

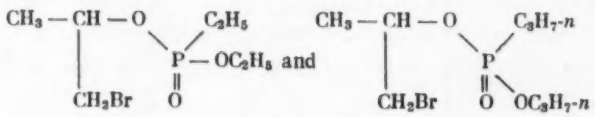
First we took some compounds with a reactive halogen – alkyl halides – for running the rearrangement reaction. The reaction between esters of propylene hydrogen phosphite and alkyl iodides was run in sealed tubes by heating within the temperature interval of 100-150°, as was usual in similar cases previously. These experiments were found to be interesting in that the products obtained from them could not be distilled since on reaching

the bath temperatures of 100-120° under 15 to 1 mm pressure a rapid decomposition set in invariably and the flask contents were strongly colored by iodide. In some cases the product decomposed spontaneously, and at times explosively, after the distillation of the solvent and a brief heating.

Owing to these facts, the following experiments with the rearrangement reaction employed alkyl bromides and chlorides for this study. The first experiments with the rearrangement were run at rather high temperatures (100° or above) with methyl, ethyl, n-propyl and n-butyl esters of propylene phosphite and the corresponding alkyl halides — methyl bromide, ethyl bromide, n-propyl bromide and n-butyl bromide. As the results of these experiments with methyl bromide at 100° and with n-butyl bromide at 150-165° we obtained the isomerization products with intact ring structures, i.e.,

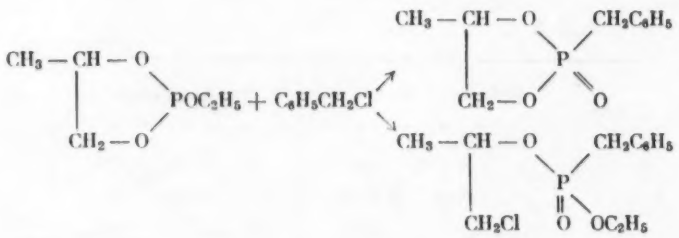


On the other hand in runs with ethyl bromide and n-propyl bromide we were able to isolate only the products with the opened ring, to which we gave provisionally the following structure:



Thus, the first series of experiments led to results in which esters which were close to each other in composition and structure (esters belonging to the same series) gave different products: some with intact cyclic grouping, others those with the opened ring. One of us had observed some similar phenomena in earlier work [2-5].

Rather unexpected results were provided by the experiments on the action of benzyl chloride on ethyl propylene phosphite, in which we obtained two products: with intact and with opened ring structure.



In order to clarify the causes of such diverse course of the reaction, we set up a series of some additional experiments which showed that the material factor which influences the final results of the reactions being studied here is the temperature of the experimental run. It was definitely shown that products with the opened ring are obtained predominantly at the lower temperatures, while those with the intact ring are obtained at the higher temperature, which fact is evident in the examples given in Table 1. It should be noted that the yields of the products were usually very low, from which it follows that these reactions are complicated by side-reactions. It is interesting to note that the isomerization proceeds comparatively smoothly and completely in the reaction of alkyl iodides on methyl and ethyl pyrocatechol phosphites, which fact undoubtedly indicates that the isomerization occurs in these cases without touching the cyclic structure of the esters [10].

We set up some special experiments to solve the question as to whether or not the addition products of alkyl halides with the opened ring could be the intermediate products in the processes of isomerization or rearrangement of the alkyl alkylene phosphites. For this purpose we prepared, in the pure state, two haloalkyl esters with opened rings, as the reaction products of methyl and ethyl bromides, respectively, with methyl and ethyl propylene phosphites; these esters were then heated in sealed tubes. The halomethyl ester was heated at 100°,

TABLE 1

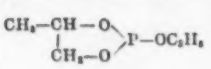
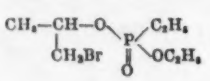
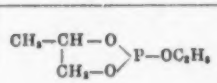
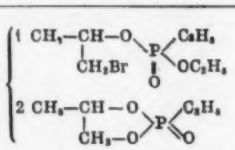
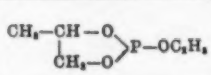
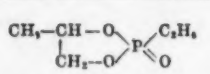
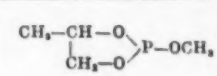
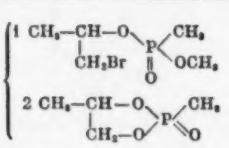
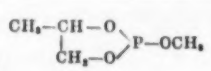
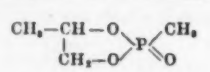
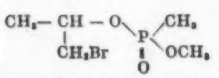
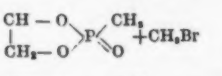
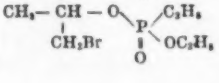
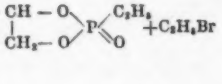
Expt. No.	Ester used	Alkyl halide used	Duration of heating	Temperature in °C	Products obtained
1		C_2H_5Br	7 hours	125	
2		C_2H_5Br	7 hours	140–150	
3		C_2H_5Br	2 hours and 45 minutes	150–160	
4		CH_3Br	10 hours	40–45	
5		CH_3Br	4 hours	100	

TABLE 2

Expt. No.	Halo ester used	Products obtained
1		
2		

while the haloethyl ester was heated to 150°. Propylene esters of methyl- and ethylphosphonic acids were isolated in small amounts as a result of fractional distillation of the reaction products (Table 2).

It is possible to conclude from these experiments that the haloalkyl esters may indeed be, under certain conditions, the intermediate products in the isomerization processes of alkyl alkylene phosphites. It was shown by later experiments with the action of the corresponding alkyl halides on the isomerized cyclic esters that the reverse reaction does not occur and that the starting materials are recovered unchanged. The excess of the alkyl halide taken for the reaction evidently improves the yield of the isomerized esters with the opened ring.

The study of these processes is greatly complicated by the fact that the haloalkyl esters used as starting materials and the corresponding cyclic esters of alkylphosphonic acids, formed by the loss of alkyl halide from them, have very close boiling points despite the considerable difference in molecular weights, if one assumes the monomeric form for the cyclic esters; thus, for example, the methyl halo ester boils at 133.5-135° (13 mm) while the propylene ester of methylphosphonic acid boils at 140-142° (13 mm).

TABLE 3

Halo Esters of Alkylphosphonic Acids

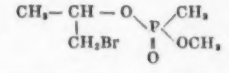
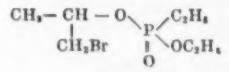
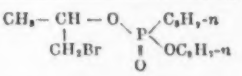
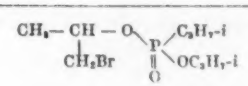
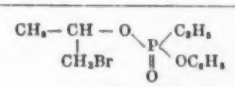
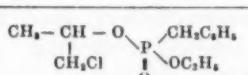
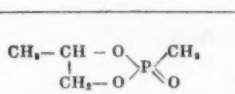
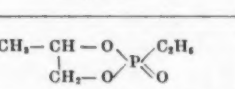
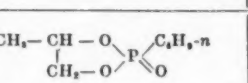
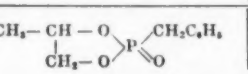
No. of product	Products obtained	B.p. in °C (p in mm Hg)	d_0^{20}	n_D^{20}	MR	
					calc.	found
1		133,5—135 (13)	1,4130	1,4535	43,93	44,19
2		134,5—135,5 (14)	1,3184	1,4558	53,17	53,38
3		121 (1)	1,2182	1,4529	62,40	63,70
4		125—127 (6)	1,2490	1,4545	62,40	62,26
5		137 (0,07)	1,3641	1,5188	68,21	68,24
6		148—150 (1)	1,1775	1,5044	70,12	69,62

TABLE 4

Cyclic Esters of Alkylphosphonic Acids

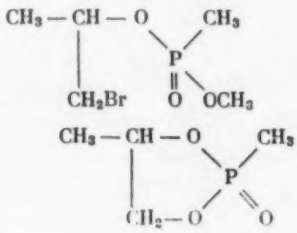
No. of product	Products obtained	B.p. in °C (p in mm Hg)	M.p. in °C	d_0^{20}	n_D^{20}	MR	
						calc.	found
1		140,5—142 (13)	—	1,2389	1,4415	29,34	29,02
2		143,5—144,5 (12)	—	1,1941	1,4444	33,40	33,90
3		121,5—123 (0,22)	—	1,1300	1,4482	43,19	42,34
4		—	122—122,5	—	—	—	—

The halo esters of alkylphosphonic acids and the cyclic esters of alkylphosphonic acids, synthesized by us, are given, with their constants, in Tables 3 and 4.

It should be noted that the halo esters formed by the ring opening may have two possible structures: the first, in which the halogen is in the primary position, and second, in which it is in the secondary position. Our

attempts to determine the site of the rupture, by the method of replacement of the halogen by the ethoxy group with the subsequent hydrolysis of the products, have failed to give any definite results so far, but all the experiments run by us appear to indicate in favor of the ring opening at the primary carbon atom. All formulas of the halo esters are provisionally shown with the ring opening at the primary carbon atom, in accord with the above material.

The remarkable fact that the halo substituted esters of alkylphosphonic acids with the opened ring boil below the products of cleavage of alkyl halide from them does require an additional study; for example:



M.p. 133,5° (13 mm) (mol.wt. 231)

B.p. 140,5° (13 mm) (mol.wt. 136)

which fact indicates that the products of the cleavage are either associated or have a different structure. A study in this direction will be continued.

EXPERIMENTAL

Action of Ethyl Bromide on the Ethyl Ester of Propylene Phosphite at the Temperature of 130-135°. 14.7 g of the ethyl ester of propylene phosphite and 10.8 g of ethyl bromide were sealed into a glass tube. The tube was heated for seven hours at 130-135°, after which it was opened. A product with b.p. 133.5-134.5° (14 mm) was isolated in the yield of 7.6 g after two fractional distillations, this amount corresponding to a 49% yield; d^{0}_{0} 1.3396, d^{20}_{0} 1.3184; $n^{20}D$ 1.4558; found MR 53.38; calculated MR for $C_7H_{16}O_3PBr$ 53.17.

Found %: P 12.76; 12.60; Br 30.67; 30.94. $C_7H_{16}O_3PBr$. Calculated %: P 12.00; Br 30.88.

Thus, the halo ester was obtained. It was a colorless liquid with a faint, rather pleasant, specific odor.

Action of n-Butyl Bromide on the n-Butyl Ester of Propylene Phosphite. 30 g of n-butyl propylene phosphite and 24 g of n-butyl bromide were heated for ten hours at 150-165°. A product with b.p. 121.5-123° (0.2 mm) was isolated after several fractional distillations in a 3 g yield, which comprised 10% of theoretical; d^{20}_{0} 1.1300; $n^{20}D$ 1.4482; found MR 42.34; calculated MR for $C_7H_{15}O_3P$ 43.19.

Found %: P 17.20; 17.08. $C_7H_{15}O_3P$. Calculated %: P 17.42.

Thus the fraction with b.p. 121.5-123° (0.2 mm) was a sufficiently pure propylene ester of n-butylphosphonic acid. The ester was a colorless liquid which was almost odorless.

Action of Methyl Bromide on the Methyl Ester of Propylene Phosphite. 20 g of methyl propylene phosphite and 14 g of methyl bromide were heated for four hours at 100°. A fraction with b.p. 140.5-142° (13 mm) was isolated after three fractional distillations in the yield of 7.5 g, which corresponded to 38% of theoretical; d^{20}_{0} 1.2389; $n^{20}D$ 1.4415; found MR 29.02; calculated MR for $C_4H_9O_3P$ 29.34.

Found %: P 22.57; 22.86. $C_4H_9O_3P$. Calculated %: P 22.87.

Thus, the fraction with b.p. 140.5-142° (13 mm) was the propylene ester of methylphosphonic acid; a colorless, transparent, almost odorless liquid.

Action of Benzyl Chloride on the Ethyl Ester of Propylene Phosphite. 16.1 g of ethyl propylene phosphite and 14 g of benzyl chloride were heated for 10 hours at 120-130°; the volume decreased slightly. The tube was heated for three additional hours at 170°; the volume decreased by an additional amount. Crystals precipitated from the third fraction after the first fractional distillation. 1.5 g of a crystalline product was isolated. A liquid product with b.p. 148-150° (1 mm) was isolated after two additional fractional distillations. The residue, amounting to 1.6 g, crystallized in the distillation pot. In all 3.1 g of the crystalline product was obtained. Colorless, shiny plates with m.p. 122-122.5° were obtained by recrystallization from carbon tetrachloride. This substance was the

propylene ester of benzylphosphonic acid, as shown by the analysis; its yield was 13% of theoretical.

Found %: P 14.78; 14.83. $C_{10}H_{13}O_3P$. Calculated %: P 14.96.

An examination of the fraction with b.p. 148-150° (1 mm): d^0_0 1.1949; d^{20}_0 1.1775; $n^{20}D$ 1.5044; found MR 69.62; calculated MR for $C_{12}H_8O_3PCl$ 70.12.

Found %: P 11.10; 11.06. $C_{12}H_8O_3PCl$. Calculated %: P 11.21.

The fraction with b.p. 148-150° (1 mm) was the mixed chloro ester of benzylphosphonic acid, for which 8.2 g was obtained, for a 30% yield. It was a viscous liquid with a faint, pleasant, specific odor.

Action of Ethyl Bromide on the Ethyl Ester of Propylene Phosphite, at the Temperature of 150-160°. 20.5 g of ethyl propylene phosphite and 15 g of ethyl bromide were heated for 2 hours and 45 minutes at 150-160° until a faint yellow color appeared. A product with b.p. 101° (0.15 mm) was isolated after three fractional distillations in the yield of 4.7 g, which was equal to 23% of theoretical; d^{20}_0 1.1941; $n^{20}D$ 1.4444; found MR 32.90; calculated MR for $C_5H_{11}O_3P$ 33.40.

Found %: P 20.16; 20.25. $C_5H_{11}O_3P$. Calculated %: P 20.66.

Thus, the examination showed that the fraction with b.p. 101° (0.15 mm) was the propylene ester of ethylphosphonic acid. It was a colorless and odorless liquid which was soluble in organic solvents.

Action of Ethyl Bromide on the Ethyl Ester of Propylene Phosphite at the Temperature of 140-145°. 67.8 g of ethyl propylene phosphite and 50 g of ethyl bromide were heated in a sealed tube for seven hours at 140-145°. Two products were isolated after several fractional distillations. The first product with b.p. 135-136.5° (15 mm), $n^{20}D$ 1.4552, d^{20}_0 1.3180, was the halo ester with the opened ring, as shown by these constants. The yield of this product was 28 g, which amounted to 25% of theoretical. The second product isolated had b.p. 143.5-144.5° (12 mm), $n^{20}D$ 1.4450, d^{20}_0 1.1946; found MR 33.90; calculated MR for $C_5H_{11}O_3P$ 33.40.

Found %: P 20.25. $C_5H_{11}O_3P$. Calculated %: P 20.66.

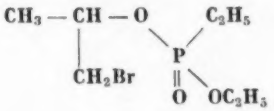
Thus, this substance was shown by its composition to be the propylene ester of ethylphosphonic acid. The yield of this ester was 7 g, which corresponded to 10% of theoretical.

Action of Methyl Bromide on the Methyl Ester of Propylene Phosphite at the Temperature of 40-45°. 9.8 g of methyl propylene phosphite and 8.5 g of methyl bromide were heated for ten hours at 40-45°. An additional heating at this temperature failed to cause a shrinkage of the volume. Two pure fractions were isolated after repeated fractional distillation under vacuum; one of these had b.p. 133.5-135° (13 mm) and was isolated in the amount of 1.9 g, comprising 11% of theoretical; d^{20}_0 1.4130, $n^{20}D$ 1.4535; found MR 44.19; calculated MR for $C_5H_{12}O_3PBr$ 43.93.

Found %: P 13.88; 13.79. $C_5H_{12}O_3PBr$. Calculated %: P 13.42.

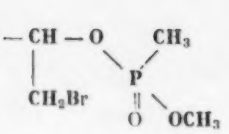
Thus, this product was the bromo ester of methylphosphonic acid – a colorless liquid with a faint, pleasant, specific odor.

The second fraction had b.p. 134-136° (11 mm), d^{20}_0 1.2383, $n^{20}D$ 1.4422. This second product was propylene ester of methylphosphonic acid, as shown by the boiling point, density and index of refraction.

Heating Ester  to the Temperature of 140-150°. 14.9 g of the bromo ester was

sealed into a tube and heated for three hours at 140-150°. The liquid acquired a brown color after the heating. 2.9 g of a liquid with b.p. 40-44° and $n^{20}D$ 1.4190 was distilled at normal pressure, these constants being indicative of ethyl bromide ($n^{20}D$ 1.4230).

Fractional distillation of the remainder under vacuum gave three fractions: 1st in the amount of 1 g, 2nd in the amount of 0.6 g, and 3rd – 6 g. All these fractions had a slight yellow color. The third fraction had b.p. 147-150° (18 mm), d^{20}_0 1.1951, $n^{20}D$ 1.4450. These constants were those of the propylene ester of ethylphosphonic acid.

Heating Ester  to the Temperature of 100°. 4.5 g of the bromo ester was sealed into a tube and heated for three hours at 100°. The liquid turned brown after the heating. The gas collected in a small amount was methyl bromide. As a result of the distillation of the remainder, there was isolated 1.6 g of a substance with b.p. 140-143° (14 mm) with the constants: $n^{20}D$ 1.4420, d^{20}_0 1.2397, which showed that this fraction was the propylene ester of methylphosphonic acid ($n^{20}D$ 1.4415, d^{20}_0 1.2389). The yield of the ester was 62% of theoretical.

Action of Ethyl Bromide on the Ethyl Ester of Propylene Phosphite. 20.5 g of ethyl propylene phosphite and 17.5 g of ethyl bromide (16% excess) were heated in a sealed tube for 2 hours and 45 minutes at 150-160°. A product with b.p. 140-142° (11 mm) was isolated after several fractional distillations in the yield of 5.9 g, which amounted to 30% of theoretical; $n^{20}D$ 1.4450. It was evident from the boiling point and the index of refraction that this was the propylene ester of ethylphosphonic acid.

Action of Benzyl Chloride on the Methyl Ester of Propylene Phosphite. 20 g of ethyl propylene phosphite and 19 g of benzyl chloride were heated for ten hours at 135-140°. Crystals precipitated after the removal of methyl chloride; these were filtered off and had m.p. 122-122.5°, after two recrystallizations from carbon tetrachloride. The Beilstein test for halogen was negative.

Found %: P 14.78; 14.83. $C_{10}H_{13}O_3P$. Calculated %: P 14.96.

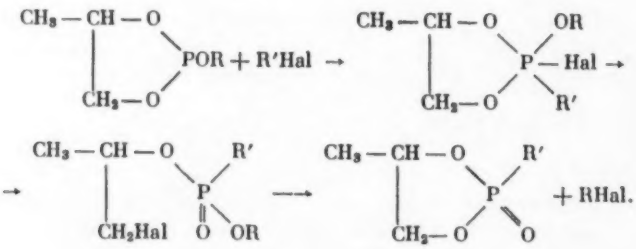
This product was the propylene ester of benzylphosphonic acid, as shown by the analysis. In all 10.8 g of it was obtained, which amounted to 35.5% of theoretical. The ester formed shiny colorless plates which were sparingly soluble in water, alcohol, benzene and ethylene chloride.

Action of Methyl Bromide (1 mole) on the Methyl Ester of Propylene Phosphite (5 moles). 12 g (5 moles) of methyl propylene phosphite and 2 g (1 mole) of methyl bromide were heated for four hours at 100°. A product with b.p. 145-150° (16 mm), $n^{20}D$ 1.4422, was isolated after opening of the tubes and a fractional distillation. The boiling point and the index of refraction showed that this was the propylene ester of methylphosphonic acid described above. Its yield was 6 g, which amounted to 50% of theoretical. Thus, methyl bromide acted as a catalyst in this experiment.

SUMMARY

1. The reaction of cyclic esters of propylene phosphite with alkyl halides (the Arbuzov rearrangement) was studied. Two types of compounds were obtained as a result of this reaction: a) cyclic propylene esters of alkylphosphonic acids and b) haloalkyl esters of alkylphosphonic acids with the opened ring.

2. The mechanism of this rearrangement, which may be represented by the following scheme, was proposed as the result of the study of the rearrangement process:



3. It was shown that the process may terminate at the stage of formation of haloalkyl esters of alkylphosphonic acids depending mainly on the temperature at which the experiment was run.

4. It was not excluded that the rearrangement of the alkyl cyclic esters may proceed in some cases along two parallel paths: the first path – along the scheme that had been accepted for trialkyl esters of phosphorous acid and the second path – with an intermediate stage of ring opening.

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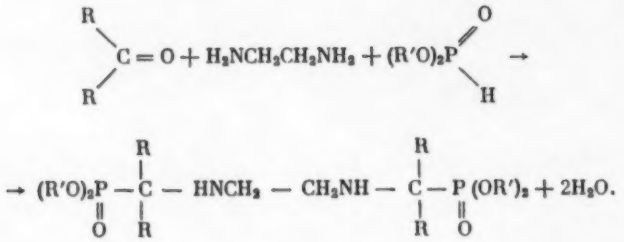
SYNTHESIS AND EVALUATION OF THE COMPLEX-FORMING ABILITY OF SOME ORGANOPHOSPHORUS COMPOUNDS

M. I. Kabachnik, T. Ia. Medved', G. K. Kozlova, V. S. Balabukha, M. M. Seniavin and L. I. Tikhonova

Highly active complex-forming substances have been discovered in recent years in the series of aminobiscarboxylic acids [1]. It was of interest, in this connection, to study the complex-forming properties of some α-aminoalkylphosphonic acids and their derivatives, whose synthesis and study have been the subject of our studies during the recent years [2]. There is little literature data on the complex-forming properties of aminoalkylphosphonic acids. Schwarzenbach, Ackermann and Ruckstuhl [3] synthesized β-aminoethylphosphono-N,N-diacetic, aminomethylphosphono-N,N-diacetic and N-methylaminomethylphosphono-N,N-diacetic acids in 1949. The authors found, by comparing the properties of these acids with those of the corresponding amino carboxylic and amino sulfonic acids, that the phosphonic acids were the stronger complex-formers. Later, the patent claims appeared from Bersworth [4] and Suter [5] concerning the preparation of ethylenediaminobis(ethylenediaminotetramethylphosphonic) acid and nicotinoylaminomethylphosphonic acid. Westerback and Martell [6] published in 1956 some data on the dissociation constants of ethylenediaminotetramethylphosphonic acid. Both Schwarzenbach and the later authors prepared the compounds described by them through the condensation of ethylenediamine with chloromethylphosphonic acid in the presence of excess alkali. The acids formed in this way were isolated in most cases in the form of sirups; the yields and the analyses of these substances are not supplied.

We tested the complex-forming properties of some aminoalkylphosphonic acids, prepared by us previously, and we also synthesized specially and tested some ethylenediaminobisphosphonic acids. The latter were prepared by the reaction of aldehydes or ketones with ethylenediamine and dialkyl hydrogen phosphites.



The resulting esters of ethylenediaminobisphosphonic acids were hydrolyzed by the action of hydrochloric acid to the corresponding free acids. We used acetone, methyl ethyl ketone, propionaldehyde and benzaldehyde as the carbonyl components. The esters of ethylenediaminobisphosphonic acids were characterized by their picrates. Only the methyl ester of ethylenediaminobisisopropylphosphonic acid was isolated in the free state. The free acids are high-melting colorless crystalline substances which are difficultly soluble in water and insoluble in organic solvents; they are readily soluble in dilute acids and bases. The characterization of the compounds prepared by us is given in Table 1.

The complex-forming ability of the aminoalkylphosphonic acids was checked by the chromatographic method, described in the paper by Seniavin and Tikhonova [7]. The activity of the complex-former was

TABLE 1

No. of compound	Formula of the compound	M.p. in °C (with decomp.)	C%		H%		P%		N%		H_2O%		Yield in % based on ethylenediamine
			found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	
1	$[(CH_3O)_2P(O)-C(CH_3)_2-NHCH_2]_2$	96—97	39,6 39,8	40,0	8,3 8,3	8,4	17,3 17,2	17,2	8,2 8,0	7,8			43
2	$[(CH_3O)_2P(O)-CH(CH_3)-NHCH_2]_2 \cdot 2C_6H_2(NO_2)_3OH$	164—165	35,2 35,4	35,2	4,6 4,6	4,4			14,2 14,2	13,7			
3	$[(C_2H_5O)_2P(O)-C(CH_3)_2-NHCH_2]_2 \cdot 2C_6H_2(NO_2)_3OH$	151	38,5 38,3	38,4	5,1 5,1	5,1	7,1 7,1	7,1	12,8 12,6	12,8			61
4	$[(C_2H_5O)_2P(O)-C(CH_3)_2-NHCH_2]_2 \cdot 2C_6H_2(NO_2)_3OH$	125—126	39,7 39,8	39,9	5,4 5,4	5,4			12,5 12,5	12,4			40
5	$[(C_2H_5O)_2-P(O)-C(C_2H_5)H-NHCH_2]_2 \cdot 2C_6H_2(NO_2)_3OH$	154	38,5 38,7	38,4	5,1 5,0	5,1			13,4 13,3	12,8			29

TABLE 1 (continued)

No. of compound	Formula of the compound	M.p. in °C (with decomp.)	C%		H%		P%		N%		H_2O%		Yield in % based on ethylene-diamine
			found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	
6	$[(C_2H_5O)_2P(O)-C(C_2H_5)H-NHCH_2]_2 \cdot 2C_6H_2(NO_2)_3OH$	193—194	44,0 44,1	44,5	4,5 4,6	4,6	6,1 5,9	6,4	11,1 11,3	11,5			47
7	$[(HO)_2P(O)-C(CH_3)_2-NHCH_2]_2 \cdot 2H_2O$	230—231	28,0 28,2	28,2	8,1 8,0	7,7	18,1 18,3	18,2	8,4 8,4	8,2	10,6	10,4	25
8	$[(HO)_2P(O)-C(C_2H_5)H-NHCH_2]_2 \cdot 2H_2O$	240	28,0 28,1	28,2	7,7 7,7	7,7	18,0 18,0	18,2	8,1 8,1	8,2	10,2	10,4	21
9	$[(HO)_2P(O)-C(C_2H_5)H-NHCH_2]_2 \cdot 2{,}5H_2O$	236	43,0 43,2	43,1	6,0 6,0	6,1	13,9 14,0	13,9	6,3 6,3	6,3	10,3	10,1	17,5

characterized by the total volume (V_{max}) of the filtrate flowing from the cationite column, with the ions of an element sorbed on the latter, beginning with the initiation of elution and ending with the attainment of the maximum concentration of the element being eluted in the filtrate. The value of V_{max} (under otherwise identical conditions) depends on the degree of stability of the complex compounds and is smaller when the latter is larger. We used ions of rare earth elements ytterbium or yttrium, containing the isotopes Yb^{175} or Y^{91}, for this experiment.

The results of the evaluation of some aminoalkylphosphonic acids are given in Table 2.

It follows from the data given in Table 2 that the group of ethylenediaminobisphosphonic acids (No. 1, 2 and 3) forms stable complex compounds with ytterbium and yttrium. Aminoalkylphosphonic acids No. 4, 5, 6 and 7 form less stable complex compounds with the ions of these elements. The remaining substances shown in the table either form poorly stable complex compounds or fail to form any.

TABLE 2

V_{max} (in ml) of Elution Curve for Yb and Y (column of cationite KU-2)

No. of compound in order	Name of acid	Concentration of the acid	
		0.05 mole/liter	0.003 mole/liter
1	Ethylenediaminobisisopropylphosphonic	< 0.25	> 25*
2	Ethylenediaminobispropylphosphonic	< 0.25	> 25*
3	Ethylenediaminobisbenzylphosphonic	< 0.25	> 25*
4	α-Aminoisopropylphosphonic	1.1	> 25
5	Hydroxybenzylphosphonic	1.9	> 25
6	N,N-Dimethylaminoisopropylphosphonic	6.4	> 25
7	α-Aminoisobutylphosphonic	> 12	> 25
8	N,N-Dimethylaminomethylphosphonic	> 25	> 25
9	α-Aminoisopropylphenylphosphinic	> 25	> 25
10	Aminobenzylphosphonic	> 25	> 25
11	Aminomethylphosphonic	> 25	> 25
12	Ethyl ester of α-aminoisopropylphosphonic acid	> 25	> 25
13	Ethyl ester of hydroxybenzylphosphonic acid	> 25	> 25
14	Ethyl ester of 1,2,5-trimethyl-4-aminopiperidyl-4-phosphonic acid	> 25	> 25
15	Ethyl ester of 1,2,5-trimethyl-4-hydroxypiperidyl-4-phosphonic acid	> 25	> 25

*A 0.006 M solution of acids No. 1, 2 and 3 elutes Y with V_{max} about 1.8 ml.

EXPERIMENTAL

Picrate of the Ethyl Ester of Ethylenediaminobisisopropylphosphonic Acid. 5.8 g (0.1 mole) of acetone was added dropwise with stirring to a mixture of 13.8 g (0.1 mole) of freshly distilled diethyl hydrogen phosphite and 3 g (0.05 mole) of ethylenediamine. The temperature of the reaction mixture rose to 111°. Then the mixture was heated on a water bath for 15 minutes at 80-85°, after which it was poured into 7-8 volumes of dry ether, with which it was then shaken vigorously. The ethereal solution was decanted from the sirupy residue (3 g) and was dried with sodium sulfate. Excess picric acid in ether was added to this ethereal solution. The picrate was recrystallized from ethyl alcohol. 27 g (61% of theoretical) of the substance with m.p. 151° was obtained.

Ethylenediaminobisisopropylphosphonic Acid. The experiment was run at first like the previous one. After the extraction of the reaction mixture with ether, the latter was distilled off and the residue was treated with 80 ml of concentrated hydrochloric acid. The solution was refluxed for seven hours after which the hydrochloric acid was distilled off under vacuum until the residue attained a constant weight. A precipitate formed after addition of excess water to the residue; this was filtered off and recrystallized from dilute hydrochloric acid. 4.2 g (25% of theoretical) of colorless, crystalline substance was obtained. It crystallized with two molecules of water, m.p. 230-231°; it was difficultly soluble in hot water, insoluble in organic solvents and readily soluble in dilute aqueous acids and alkalies.

Methyl Ester of Ethylenediaminobisisopropylphosphonic Acid, and Its Picrate. This was prepared from 11 g (0.1 mole) of dimethyl hydrogen phosphite, 3 g (0.05 mole) of ethylenediamine in 25 ml of benzene and 5.8 g (0.1 mole) of acetone in 5 ml of benzene, similarly to the run with the diethyl hydrogen phosphite. Two layers formed after the completion of the reaction: the upper one – the benzene layer – was separated and the lower layer was washed with benzene. The benzene solutions were combined and dried over sodium sulfate. The residue, after the distillation of benzene, crystallized yielding 8.0 g (43% of theoretical) of the product. This had m.p. 96-97° after a recrystallization from a mixture of benzene and petroleum ether. The picrate was recrystallized from 80% ethyl alcohol; m.p. 164-165°.

6.3 g of the methyl ester of ethylenediaminobisisopropylphosphonic acid was evaporated down twice with 30 ml of 1:1 hydrochloric acid on a steam bath. After the removal of hydrochloric acid, the residue was treated with water until crystals appeared. 3.6 g of the substance with m.p. 230-231° was obtained after recrystallization.

Picrate of the Ethyl Ester of Ethylenediaminobisisobutylphosphonic Acid. This was prepared from 13.8 g (0.1 mole) of diethyl hydrogen phosphite, 3.0 g (0.05 mole) of ethylenediamine and 7.2 g of methyl ethyl ketone, as described in the first experiment. The product with m.p. 125-126° was obtained after recrystallization from ethyl alcohol; yield: 18 g (40%). A sirup which could not be made to crystallize was obtained after hydrolysis of the ethyl ester of ethylenediaminobisisobutylphosphonic acid with hydrochloric acid.

Picrate of the Ethyl Ester of Ethylenediaminobispropylphosphonic Acid. This was prepared from 6.9 g (0.05 mole) of diethyl hydrogen phosphite, 1.5 g (0.025 mole) of ethylenediamine and 2.9 g (0.05 mole) of propionaldehyde. 6.3 g (29% of theoretical) of the picrate with m.p. 156° was obtained after recrystallization from ethyl alcohol.

Ethylenediaminobispropylphosphonic Acid. This was prepared from 13.8 g (0.1 mole) of diethyl hydrogen phosphite, 3 g (0.05 mole) of ethylenediamine and 5.8 g (0.1 mole) of propionaldehyde. A colorless crystalline substance with m.p. 240° was obtained after the hydrolysis of the reaction product with hydrochloric acid and recrystallization from hydrochloric acid; yield: 1.8 g (21% of theoretical).

Picrate of the Ethyl Ester of Ethylenediaminobisbenzylphosphonic Acid. This was prepared from 11.5 g (0.08 mole) of diethyl hydrogen phosphite, 2.5 g (0.04 mole) of ethylenediamine and 8.8 g (0.08 mole) of benzaldehyde. There was obtained 18 g (47% of theoretical) of the picrate with m.p. 193-194° after recrystallization from ethyl alcohol.

Ethylenediaminobisbenzylphosphonic Acid. This was prepared from 11.5 g (0.08 mole) of diethyl hydrogen phosphite, 2.5 g (0.04 mole) of ethylenediamine and 8.8 g (0.08 mole) of benzaldehyde, as described in the second experiment. There was isolated 3.14 g (17.5% of theoretical) of colorless needles after hydrolysis and recrystallization from hydrochloric acid; m.p. 236°; the product crystallized with 2.5 molecules of water.

SUMMARY

1. It was shown that the formation of esters of ethylenediaminobisalkylphosphonic acids occurs in the reaction of ethylenediamine with dialkyl hydrogen phosphites and aldehydes or ketones; hydrolysis of these esters may serve to yield the corresponding free acids.

2. The complex-forming ability of the resulting ethylenediaminobisalkylphosphonic acids and that of several other aminoalkylphosphonic acids, synthesized earlier, was evaluated by the chromatographic method. It was found that ethylenediaminobisalkylphosphonic acids form stable complex compounds with ytterbium and yttrium.

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CONCERNING THE REACTION OF METALS WITH HYDROXYL-CONTAINING ORGANOSILICON COMPOUNDS

K. A. Andrianov and A. A. Zhdanov

Organosilicon compounds containing a hydroxyl group bound to the silicon atom are noted for their high reactivity toward elements which are capable of positive polarization or of formation of positive ions. Thus, for example, triethylsilanol is distinguished by greater reactivity in respect to metallic sodium than is possessed by its organic analog – tert-heptyl alcohol [1]. It was shown in our previous papers [2, 3] as well as in those of other workers [4], that triethylsilanol is able to react with aluminum, forming aluminum triethylsilanoxide with evolution of hydrogen. The high reactivity of the hydroxyl-bearing organosilicon compounds relative to metals is explained by the fact that the silicon atom in these compounds has a clearly defined positive polarity, which in turn causes the great mobility of the hydrogen atom of the hydroxyl group connected to the silicon atom.

It was of interest for us to examine the reactivity of some polymeric organosilicon compounds containing hydroxyl groups at the silicon atom with respect to metals. It is known that polymeric hydroxyl-bearing organosilicon compounds are able to condense on being heated, forming products with a still higher degree of polymerization. If the condensation reaction of organosilicon compounds is run in the presence of metals, the hydroxyl groups of the polymer would be able to react in two directions. If the rate of the intermolecular condensation reaction of the hydroxyl groups exceeds the rate of the reaction of the metal with the hydroxyl group, the process would be directed mainly in the direction of formation of the purely organosilicon polymer. With the inverted ratio of the reaction rates, a polymer containing metallosiloxane links should be formed as the result of the process. Thus, the reactivity of the hydroxyl-containing organosilicon compounds in respect to metals would be determined by the nature of the compound and by the stability of the hydroxyl groups in the reaction of intermolecular condensation. One should expect that the organosilicon compounds containing more than one group at the silicon atom would display a low reactivity toward metals since such compounds condense readily, forming polymers which are practically devoid of hydroxyl groups. If for this reaction one takes compounds which contain not more than one hydroxyl group at the silicon atom, such compounds would react relatively readily with metals, forming poly(organometallosiloxanes).

Our studies showed that diethylsilanediol hardly reacts at all with metallic aluminum and undergoes mainly the intermolecular condensation reaction, forming poly(diethylsiloxanes). 1,3-Dihydroxytetraethyldisiloxane reacts readily with aluminum and magnesium, forming poly(ethylmetallosiloxanes). Polyphenylsiloxanes, containing a small number of hydroxyl groups, turned out to be relatively more reactive toward aluminum than was diethylsilanediol. The data given in Table 1 characterize the average reactivity of hydroxyl-containing organosilicon compounds toward various metals.

The data shown in Table 1 permit us to express the process of the reaction of 1,3-dihydroxytetraethyldisiloxane with metals by the following approximate reaction schemes:

$$HOSi(C_2H_5)_2OSi(C_2H_5)_2OH + 2Na \rightarrow NaOSi(C_2H_5)_2OSi(C_2H_5)_2ONa + H_2;$$

$$2HOSi(C_2H_5)_2OSi(C_2H_5)_2OH + 2Na \rightarrow NaOSi(C_2H_5)_2OSi(C_2H_5)_2OH + H_2;$$

$$3HOSi(C_2H_5)_2OSi(C_2H_5)_2OH + 2Mg \rightarrow$$

$$\rightarrow HOSi(C_2H_5)_2OSi(C_2H_5)_2OMgOSi(C_2H_5)_2OSi(C_2H_5)_2OMgOSi(C_2H_5)_2OSi(C_2H_5)_2OH + 2H_2;$$

$$6HOSi(C_2H_5)_2OSi(C_2H_5)_2OH + 2Al \rightarrow Al[OSi(C_2H_5)_2OSi(C_2H_5)_2OH]_3 + 3H_2.$$

TABLE 1

No. of compound	Substance	Metal	Am't. of reacted OH groups, in % of total OH groups
1	$(C_2H_5)_3SiOH$	Al	88,0
2	$(C_2H_5)_2Si(OH)_2$	Al	1,2
3	$HOSi(C_2H_5)_2OSi(C_2H_5)_2OH$	Na	66,4
4	$HOSi(C_2H_5)_2OSi(C_2H_5)_2OH$	Mg	62,7
5	$HOSi(C_2H_5)_2OSi(C_2H_5)_2OH$	Al	58,2
6	Polyphenylsiloxane	Na	88,2
7	"	Na	71,3
8	"	Al	9,0
9	"	Al	5,5

EXPERIMENTAL

Diethylsilanediol was synthesized by the method which had been proposed by Leznov and co-workers, by hydrolysis of diethyldiacetoxysilane. The product had m.p. 95.5° after recrystallization from a 2:1 mixture of ether and benzene.

1,3-Dihydroxytetraethyldisiloxane was prepared by hydrolysis of diethyldiethoxysilane by the following technique: 210 g (1.19 moles) of freshly distilled diethyldiethoxysilane (b.p. 156-157°), 210 g of water and a drop of 15% hydrochloric acid were heated for four hours at 75-90°. After completion of the hydrolysis, the water layer was separated, the organic layer was thoroughly washed with water and dried with potassium carbonate. The dried product was heated under vacuum for three hours at 70°, after which it was dried in a vacuum desiccator over calcium chloride to constant weight. In all 116 g of the product (88% of theoretical) was obtained.

Found %: OH 15.8 (by Chugaev-Tserevitinov method); M (cryoscopically in benzene) 215; $C_8H_{22}O_3Si_2$.
Calculated %: OH 15.3; M 222.

Polyphenylsiloxane resins. 212 g (1 mole) of phenyltrichlorosilane dissolved in 212 g of toluene was introduced, with intense stirring and cooling, into a mixture of 424 g of water and 212 g of dibutyl ether. The water layer was separated after completion of the addition, the organic layer was washed with water until neutral, dried with sodium sulfate and filtered from the drying agent. The solvent was distilled from the dried organic layer up to the temperature of 70° at 30 mm pressure. The resin was dried in a vacuum drier at 100° and 10 mm to constant weight for the final removal of solvent residues. 117 g of the resin (91% of theoretical) was obtained.

Found %: Si 20.0; HO 7.6.

A second sample of the poly(phenylsiloxane) resin was prepared by hydrolysis of phenyltriethoxysilane by an aqueous solution of hydrochloric acid. A mixture of 240 g (1 mole) of phenyltriethoxysilane, 240 g of toluene and 240 g of 10% hydrochloric acid was boiled for one hour, after which the aqueous layer was separated and the organic layer was treated as described above. 103 g of resin was obtained as a result, this amount corresponding to an 80% yield of theoretical.

Found %: Si 20.5; OH 5.9; OC_2H_5 4.2.

Reaction of metals with organosilicon compounds. A gas burette with saturated aqueous salt solution for the fluid was used in the reaction. The burette was connected to a test tube in which the reaction was run. The reaction was run with or without a solvent (xylene), depending on the nature of the substance used and the metal taken for the reaction, which was run at various temperatures with various durations of heating. The test-tube was cooled to the temperature of the water jacket around the burette, after completion of the reaction, after which the volume of generated hydrogen was measured and this was corrected to standard conditions by the usual methods, making the correction for vapor pressure of the solution in the burette and that of the solvent, if the latter was used.

Diethylsilanediol and aluminum. The reaction was run in the absence of a solvent for two hours at 150°. The results are given in Table 2.

TABLE 2

Expt. No.	Sample of diethylsilanediol, in g	Vol. of H_2 (at normal conditions) in ml	Amt. of reacted OH groups in %
1	4,0845	8,4	1,1
2	2,0835	3,5	0,9
3	2,1104	5,9	1,5
4	2,3820	5,3	1,2

TABLE 3

Expt. No.	Sample of 1,3-dihydroxytetraethyldisiloxane, in g	Vol. of H_2 (at normal conditions) in ml	Amt. of reacted OH groups in %
1	0,7182	62	86,2
2	0,9864	72	72,8
3	1,0904	56	51,2
4	1,0840	68	62,6
5	1,1444	68	59,3

1,3-Dihydroxytetraethyldisiloxane and sodium. The reaction was run in the presence of 1 ml of xylene for 1.5 hours at 130°. The metallic sodium, just like the other metals in all remaining experiments, was taken in a considerable excess over the theoretical amount. The results are given in Table 3.

1,3-Dihydroxytetraethyldisiloxane and magnesium. The reaction was run in the absence of a solvent for 1.5 hours at 250°. Magnesium was used in the form of fine freshly-made powder. The results of the experiments are given in Table 4.

1,3-Dihydroxytetraethyldisiloxane and aluminum. The reaction was run in the absence of a solvent by heating a fluid mixture of 1,3-dihydroxytetraethyldisiloxane and aluminum. The reaction temperature was 250° and its duration 1.5 hours. The results of the experiments are given in Table 5.

TABLE 4

Expt. No.	Sample of 1,3-dihydroxytetraethyldisiloxane in g	Vol. of H_2 (at normal conditions), ml	Amt. of reacted OH groups in %
1	1,1040	70	63,3
2	0,9140	47	51,4
3	0,9534	66	69,2
4	1,03 0	67	64,5
5	1,0570	69	65,2

TABLE 5

Expt. No.	Sample of 1,3-dihydroxytetraethyldisiloxane in g	Vol. of H_2 (at normal conditions), ml	Amt. of reacted OH groups in %
1	1,0500	60	57,0
2	0,9796	58	59,1
3	1,1480	51	44,3
4	1,0410	64	61,4
5	0,9242	64	69,1

TABLE 6

Expt. No.	Type of resin	Metal	Sample of resin in g	Vol. H_2 (at normal conditions) in ml	Amount of reacted OH groups in %
1	E	Na	0,3146	11	90,9
2	E	Na	0,4021	13	35,5
3	Kh	Na	0,3182	11	68,8
4	Kh	Na	0,3407	12	73,7
5	E	Al	1,1 60	4,3	9,3
6	E	Al	1,2844	4,4	8,8
7	Kh	Al	0,7908	1,9	4,8
8	Kh	Al	0,9491	3,0	6,3

Poly(phenylsiloxane) resins and the metals. The reaction with aluminum was run without a solvent while that with sodium was run in the presence of toluene. The temperature and the duration of the process were 200°

and 2 hours in the first case, respectively, and 100° and 2 hours in the second case. The results of the experiments are given in Table 6.

SUMMARY

1. The reaction of metals – sodium, magnesium and aluminum – with hydroxyl-containing organosilicon compounds – diethylsilanediol, 1,3-dihydroxytetraethyldisiloxane and poly(phenylsiloxane) resins – was studied. It was shown that during the reaction of these compounds with metals there occurs an evolution of hydrogen and formation of the metallosiloxane bond.

2. The reactivity of hydroxyl-containing organosilicon compounds is determined by the stability of the hydroxyl groups in the latter. Compounds which readily enter the intermolecular condensation reaction do not react with the metals. Compounds containing stable hydroxyl groups react with metals readily.

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THE RELATIONSHIP BETWEEN THE STRUCTURE OF SOME ORGANO-SILICON COMPOUNDS AND THEIR MOLAR REFRACTIONS

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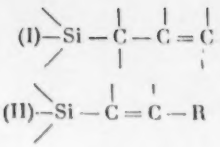
The existing methods of calculation of molar refractions (MR) of organic compounds are based on the principle of summation of the values assigned to the individual atoms or individual bonds which form the molecule of the organic compound. However, the additivity principle of atomic refractions is often valid only in such a case in which the structural peculiarities of the molecule are taken into account. Thus, while the atomic refractions of C and H may be regarded as practically constant in the majority of organic compounds, several values of the atomic refraction must be introduced for the atomic refraction of such elements as O, N, S and P, depending on the class of compounds studied [1]. It is possible to preserve the principle of additivity of MR for the unsaturated compounds by the introduction of special constant values – increments for the double and the triple bonds – concepts which lack a physical sense of meaning [1]. The system of bond refractions proposed by Denbing [2] is free of many of the above-listed defects, in contrast to the system of atomic refractions; this system is more universal, more accurate and is undoubtedly better founded [1].

The calculation of molar refractions of organosilicon compounds by the method of summation of atomic refractions is completely unacceptable, as is shown experimentally, since it is difficult or even impossible to predict always the value of the atomic refraction of Si in a new compound. Bigden [3] discovered in 1916 that the atomic refraction of silicon may have any value from 3.23 to 8.5 ml depending on the class of the compound. Even within the limits of a given class of silicohydrocarbons the atomic refraction of silicon changes materially, as for example for $(C_2H_5)_3SiR$ and $(CH_3)_3SiR$ it changes from 7.12 to 7.47 ml respectively [4]. The wide range of fluctuations of the atomic refraction of silicon in organosilicon compounds is explained by the greater polarizability of the valence electrons of the Si atom and the easy deformation of its electron shells under the influence of other elements bound to the Si atom. These peculiarities appear in various degrees on other organometallic compounds as well, such as those which contain tin, germanium, lead and other metals and metalloids.

Sauer [5] and Warrick [6] calculated the values of bond refractions of silicon with some other elements, using the values of Denbing's bond refraction. The bond refractions proposed by Warrick (Table 2) have received a universal acceptance since their use results in a satisfactory agreement of the found and the calculated molar refractions for any class of organosilicon compounds. Vogel [7] recently published an extensive tabulation of refined bond refractions, which differ somewhat from the values found by Denbing, which naturally led to an alteration of the values of the bond refractions of silicon [8]. However, the application of the refined bond refractions of Vogel (Table 3) does not have any advantages in the calculation of MR of organosilicon compounds over the values proposed for this purpose by Denbing and Warrick. Examples of the calculations are given in Table 1. We repeat that the use of Denbing's and Warrick's bond refractions yields excellent agreement between the found and the calculated MR for many hundreds of organosilicon compounds and for this reason these values have been used by all workers up to the present time.

At the same time we discovered certain classes of organosilicon compounds in which the systematic deviation of the calculated and the found MR exceeded the experimental error and could not be attributed to the contamination of the substance. This was noted at first among compounds containing ethyl and allyl radicals [9], after which some new facts were uncovered [10]. At the present time it appears possible to us to formulate the following rule: the exaltation of molar refraction (ΔMR) is observed in those compounds in which one of the following atomic groupings is present:



Alkenylsilanes with the β-position of the double bond relative to the Si atom, i.e., compounds having a conjugated system of polarized Si—C bond with the C=C double bond (σ-π conjugation [11]), belong to the compounds with the (I) grouping. The above rule is displayed particularly clearly in the homologous series of silicohydrocarbons with a terminal primary-secondary double bond: $R_3Si(CH_2)_nCH=CH_2$. The exaltation of molar refraction is not observed for the vinylsilanes (n = 0), for γ-butenylsilanes (n = 2) or for other alkenylsilanes with n greater than 2. In the case of allylsilanes (n = 1), an exaltation of MR equal to +0.18 (see Table 5) is constantly observed. It was noted [9] that ΔMR is an additive magnitude in this case, i.e., it is proportional to the increased number of the allyl radicals at the silicon atom. For example, the deviation of the calculated and the found MR in $(CH_3)_2Si(CH_2CH=CH_2)_2$ is +0.34, in $CH_3Si(CH_2CH=CH_2)_3$ it is about 0.55 and, finally, in $Si(CH_2CH=CH_2)_4$ it is +0.72, i.e., with comparison of ΔMR for $Me_3SiCH_2CH=CH_2$, the MR exaltation rises correspondingly by 2, 3 and 4-fold.

A characteristic peculiarity of compounds with the conjugated unsaturated bonds is the decrease of ΔMR if an alkyl group appears at the central atoms of the conjugated system [12]. We succeeded in finding a similar phenomenon among the methallylsilanes [10] in which the exaltation of MR is hardly discernible (+0.05) in comparison with the allylsilanes, despite the β-position of the double bond ($SiCH_2C(CH_3)=CH_2$). Evidently, the aromatic silicohydrocarbons may be regarded as compounds falling into grouping (I) with n = 1, i.e., those having the σ-π conjugation, if these have the structure $R_3Si(CH_2)_nC_6H_5$. Actually, if a benzyl radical (n = 1) is connected to the silicon atom, an exaltation of MR is observed which is equal to about 0.5. For compounds having the phenyl (n = 0) or β-phenylethyl radicals (n = 2), the exaltation of MR was practically unobservable (Table 5) [13]. It should be noted that the existence of exaltation of MR in organosilicon compounds, as discovered by us, specifically among allylsilanes and other alkenylsilanes, is accompanied by increased reactivity and a series of other physical peculiarities of these compounds [14].

The second group of compounds which have a considerable exaltation of MR are the compounds containing grouping (II) in their structure, i.e., SiC=CR, where R may be Cl, CH_3, C_2H_5, C_6H_5 and even SiR_3. It is interesting to note that the isomeric compounds with grouping SiCR=C do not have an exaltation at all or have it in smaller measure only (Table 5). Actually, if the exaltation of MR for $Me_3SiC(=CH_2)SiMe_3$ is equal to about 0.2, it reaches the value of 0.8 for $Me_3SiCH=CHSiMe_3$. Such a divergence of the calculated and the found MR leads to the thought of an insufficiently pure compound. This circumstance led to a special study which showed that the large exaltation of MR is the peculiarity of the given structures [15]. An especially large exaltation of MR is found among compounds with the $SiCH=CR_2$ grouping. For example, trimethylisocrotylsilane has ΔMR 0.5, while methyltri-isocrotylsilane has the value of 1.36 ml, i.e., in this case the complete additivity of ΔMR for the isocrotyl radical is preserved. Isocrotylsilanes, like other compounds with large ΔMR cited above, have a clearly increased reactivity [14]. And, finally, we discovered an alternation in the presence and the absence of exaltation of MR among organosilicon compounds having methyl, ethyl, propyl and butyl radicals. In case of methyl and propyl radicals bound to the silicon atom, there is no exaltation of MR at all (Table 5). In the presence of ethyl and butyl radicals, an exaltation of MR is observed and this is proportional to the number of these radicals as in the examples mentioned above. There is an especially noticeable ΔMR with the ethyl radical (0.12); for example in $(C_2H_5)_4Si$ the ΔMR reaches the value of 0.48 ml. The exaltation of MR for the butyl radical, which is equal to about 0.08, already lies within the limits of the error of the measurements and is shown noticeably only in compounds with a large number of butyl radicals. Undoubtedly, the alternation of ΔMR, discovered in this series of radicals (which shows the presence or the absence of conjugation), may be accompanied by an alternation of the chemical properties of the compounds which contain these radicals. The first examples which confirm this position were found in the polymerization of trimethyl and triethylalkenylsilanes; the polymerization of the latter proceeds more completely and deeply [16].

We give in Table 4 the values of the group refractions of the series of radicals bound to the silicon atom, as calculated by us from the experimental data. We note that Warrick [6] had calculated the group refraction

TABLE 1

Formula of the compound	MR		
	found	calculated	
		according to Warrick	according to Vogel
$(CH_3)_3SiCH=CH_2$	34,49	34,44	34,362
$Si(CH=CH_2)_4$	46,87	46,92	46,872
$Si(CH_2CH_3)_4$	48,34	48,80	48,784
$(CH_3)_3SiCH_2CH_2CH_3$	39,49	39,54	39,488
$(CH_3)_2Si(CH_2-CH=CH_2)_2$	48,20	47,86	47,828
$HSi(CH_2CH_2CH_2CH_3)_3$	67,48	67,58	67,646
$(CH_3)_3SiC_6H_5$	50,10	50,10	50,352
$Si(CH_2CH=CH_2)_4$	66,16	65,44	65,464

TABLE 2

Values of bond refractions according to Denbing and Warrick

(C — C)	1,25	(C — Br)	9,37	(Si — C_{al})	2,50
(C = C)	4,16	(C — J)	14,55	(Si — C_{ar})	2,56
(C ≡ C)	6,40	(C = O)	3,38	(Si — Si)	5,65
(C — H)	1,69	(C_{ar} = C_{ar})	2,73	(Si — H)	3,20
(N — H)	1,81	(C_{Na} = C_{Na})	2,78	(Si — F)	1,50
(O — H)	1,73	(C ≡ N)	4,95	(Si — Cl)	7,20
(C — N)	1,54	(C = N)	3,90	(Si — Br)	10,20
(C — O)	1,51	(S — H)	4,93	(Si — N)	2,00
(C — F)	1,72	(C — S)	4,55	(Si — S)	6, 5
(C — Cl)	6,53	(S — S)	8,15		
		(Si — O)	1,75		

TABLE 3

Values of bond refractions according to Vogel

(C — H)	1,676	(C — O) Acetals	1,46	(N — H)	1,76
(C — C)	1 ,296	(C = O) Methyl ketone	3,32	(N — O)	2,43
(C — C) Cyclopropane	1,50	(C — O)	3,49	(N → O)	1,78
(C — C) Cyclobutane	1,38	(C — S)	4,61	(N = O)	4,00
(C — C) Cyclopentane	1,26	(C = S)	11,91	(N = N)	4,12
(C — C) Cyclohexane	1,27	(C — N)	1,57	(Si — C)	2,52
(C — C) Aromatic	2,69	(C = N)	3,75	(Si — C_{ar})	2,93
(C = C)	4,17	(C ≡ N)	4,82	(Si — F)	1,7
(C ≡ C) Terminal	5,87	(N — N)	1,99	(Si — Cl)	7,11
(C ≡ C) Nonterminal	6,24	(OH) Alcohols	1,66	(Si — Br)	10,08
(C — F)	1,45	(O — H) Acids	1,80	(Si — Si)	5,89
(C — Cl)	6,51	(S — H)	4,80	(Si — O)	1,80
(C — Br)	9,39	(S — S)	8,11	(Si — H)	3,17
(C — I)	14,61	(S — O)	4,94	(Si — S)	6,14
(C — O) Ether	1,54	(S → O)	0,20	(Si — N)	2,16

only for the methyl and phenyl radicals. The use of the values of group refractions which are proposed by us for the calculation of MR is considerably more convenient and, most important, gives more accurate results since the group refractions consider the exaltation of MR. In Table 4 we give the group refractions mainly to those radicals which possess a large exaltation of MR. For example the real group refraction of the isocrotyl radical is 21.44 ml, while that calculated on the basis of Warrick's bond refractions is 20.99 ml. Naturally the calculation of MR by the method of summation of bond refractions in these cases leads to incorrect results. Introduction of

TABLE 4

Values of group refractions

(Si−CH_3)	7,57	(Si−CH=CHC_6H_5)	38,34
(Si−C_6H_5)	12,08	(SiC≡CH)	37,20
(Si−n-C_3H_7)	16,83	| C_6H_5	
(Si−n-C_4H_9)	21,38		
(Si−C_6H_5)	27,39	(Si−$CH_2CHCH_2CH=CH_2$)	30,25
(Si−$CH_2C_6H_5$)	32,20	| CH_3	
(Si$CH_2CH_2C_6H_5$)	36,44		
(Si−CH=CH_2)	11,73	(Si−α-C_7H_{10})	45,25
(Si−$CH_2CH=CH_2$)	16,54	(Si−Br)	10,30
(Si−$CH_2CH_2CH=CH_2$)	20,90	(Si−OH)	3,5
(Si−CH=$CHCH_3$)	16,71	(Si−NCS)	17,40
(Si−C=CH_2)	16,36	(Si−CH_2Cl)	12,41
| CH_3		(Si−CH_2I)	20,43
		(Si$CH_2CH_2CH_2Cl$)	21,67
(Si−CH−C=CH)	21,04	(SiCH=CHCl)	16,87
| CH_3		(SiCCl=CH_2)	16,47
		(SiCH_2SCN)	19,93
(Si−C≡C−CH=CH_2)	20,63	(Si−CH_2SH)	15,22
(Si−CH=CH−CH=CH_2)	21,80	(Si−CH_2OH)	9,12
(Si−CH=C−CH_3)	21,44	(Si−$CH_2O_2CCH_3$)	18,60
| CH_3		[(Si−$CH_2CH_2CH_2S_2P(OCH_3)_2$]	53,35
		(Si−$CH_2CH_2CH_2SCOCH_3$)	34,65

TABLE 5

Formula of the compound	MR					Reference
	found	calc. by [6]	Δ	calc. by us	Δ	
$(CH_3)_3SiCH=CH_2$	34,49	34,44	+0,05	34,44	+0,05	[17]
$(C_2H_5)_3SiCH=CH_2$	47,99	48,33	−0,34	47,97	+0,02	[18]
$(n\text{-}C_3H_7)_3SiCH=CH_2$	62,25	62,22	+0,03	62,22	+0,03	[17]
$(CH_3)_2Si(CH=CH_2)_2$	38,52	38,60	−0,08	38,60	−0,08	[19]
$Si(CH=CH_2)_4$	46,87	46,92	−0,05	46,92	−0,05	[20]
$(CH_3)_2SiCH_2CH=CH_2$	39,20	39,07	+0,13	39,25	−0,05	[21]
$(C_2H_5)_2SiCH_2CH=CH_2$	52,72	52,96	−0,24	52,78	−0,06	[22]
$Cl_3SiCH_2CH=CH_2$	38,18	37, 5	+0,23	38,14	+0,04	[23]
$(CH_3)_2Si(CH_2CH=CH_2)_2$	48,20	47,86	+0,34	48,22	−0,02	[24]
$CH_3Si(CH_2CH=CH_2)_3$	57,20	56,65	+0,55	57,19	+0,01	[24]
$Si(CH_2CH=CH_2)_4$	66,16	65,44	+0,72	66,16	0,00	[25]
$(CH_3)_2SiCH_2CH_2CH=CH_2$	43,66	43,70	−0,04	43,70	−0,04	[26]
$(C_2H_5)_2SiCH_2CH_2CH=CH_2$	57,22	57,59	−0,37	57,23	−0,01	[18]
$(CH_3)_2C_6H_4SiCH_2CH_2CH=CH_2$	48,22	48,33	−0,11	48,21	+0,01	[18]
$(CH_3)_2SiCH_2CHCH_2CH=CH_2$	52,91	52,96	−0,05	52,96	−0,05	[27]
| CH_3						
$(C_6H_5)_2SiCH_2CHCH_2CH=CH_2$	66,53	66,85	−0,32	66,49	+0,04	[24]
| CH_3						
$H(CH_3)_2SiCH_2C=CH_2$	39,42	39,33	+0,09	39,38	+0,04	[28]
| CH_3						
$(CH_3)_2SiCH_2-C=CH_2$	43,81	43,70	+0,11	43,75	+0,06	[28]
| CH_3						
$(C_6H_5)_2SiCH_2C=CH_2$	57,27	57,59	−0,32	57,28	−0,01	[24]
| CH_3						
$CH_3Si(CH_2C=CH_2)_3$	70,66	70,54	+0,12	70,69	−0,03	[26]
| CH_3						
$Si(CH_2C=CH_2)_4$	84,27	83,96	+0,31	84,16	+0,11	[26]
| CH_3						

TABLE 5 (continued)

Formula of the compound	MR					Reference
	found	calc. by [6]	Δ	calc. by us	Δ	
$(CH_3)_3SiC_6H_5$	49,99	49,95	+0,04	4 ,95	+0,04	[13]
$(CH_3)_2SiCH_2C_6H_5$	54,96	54,52	+0,46	54,91	+0,05	[13]
$(CH_3)_2SiCH_2CH_2C_6H_5$	59,22	59,15	+0,07	59,15	+0,07	[13]
$(C_2H_5)_3SiC_6H_5$	63,62	63,99	−0,37	63,63	−0,01	[13]
$(C_2H_5)_2SiCH_2C_6H_5$	68,38	68,41	−0,04	68,44	−0,06	[13]
$(C_2H_5)_2SiCH_2CH_2C_6H_5$	72,55	73,04	−0,49	72,68	−0,13	[13]
$Cl_2SiCH=CHCl$	38,37	38,17	+0,2	38,47	−0,1	[29]
$Cl_2SiCCl=CH_2$	38,01	38,17	−0,16	38,07	−0,06	[29]
$(CH_3)_2SiCH_2-CHCl$	39,63	39,28	+0,35	39,58	+0,05	[29]
$(CH_3)_2SiC(Cl)=CH_2$	39,14	39,28	−0,14	39,18	−0,04	[30]
$(C_2H_5)_2Si(Cl)=CH_2$	52,64	53,17	−0,53	52,71	−0,07	[20]
$n\text{-}C_3H_7(CH_3)_2SiCH=CHC_6H_5$	69,96	67,94	+2,02	70,31	−0,35	[17]
$(CH_3)_2SiCH=CHC_6H_5$	61,39	58,68	+2,71	61,05	+0,34	[29]
$(CH_3)_2SiC(C_6H_5)=CH_2$	59,96	58,68	+1,28	59,91	+0,01	[17]
$(CH_3)_2SiCH=CHSi(CH_3)_3$	58,79	57,96	+0,80	—	—	[15]
$(CH_3)_2SiC(Si(CH_3)_3)=CH_2$	57,76	57,96	−0,20	—	—	[15]
$(CH_3)_2SiCH=CHCH_3$	39,37	39,07	+0,30	39,02	+0,05	[31]
$(C_2H_5)_2SiCH=CHCH_3$	53,13	52,96	+0,17	52,95	+0,18	[31]
$Cl_2SiCH=CHCH_3$	38,39	37,96	+0,43	38,31	+0,08	[31]
$(CH_3)_2SiC(CH_3)=CH_2$	39,13	39,07	+0,05	39,07	+0,04	[31]
$(C_2H_5)_2SiC(CH_3)=CH_2$	52,58	52,96	−0,38	52,60	−0,02	[31]
$(CH_3)_2SiCH=C(CH_3)-CH_3$	44,20	43,70	+0,50	44,15	+0,05	[31]
$(CH_3)_2Si(CH=C(CH_3)-CH_3)_2$	57,83	57,12	+0,71	58,02	−0,19	[31]
$CH_3Si(CH=C(CH_3)-CH_3)_3$	71,50	70,54	+1,36	71,89	−0,01	[31]
$C_6H_5(CH_3)SiCH=C(CH_3)-CH_3$	57,80	57,59	+0,21	57,68	+0,12	[31]
$C_6H_5(CH_3)_2SiCH=C(CH_3)-CH$	48,64	48,33	+0,31	48,66	−0,02	[20]
$Cl_2SiCH=C(CH_3)-CH_3$	42,99	42,59	+0,40	43,04	−0,05	[29]
$(CH_3)_2SiC\equiv C-CH=CH_2$	43,35	42,09	+1,26	43,34	+0,01	[32]
$(C_2H_5)_2SiC\equiv C-CH=CH_2$	56,83	55,98	+0,85	56,87	−0,04	[32]
$(n\text{-}C_3H_7)_2SiC\equiv C-CH=CH_2$	71,13	69,87	+1,25	71,12	+0,01	[32]
$(n\text{-}C_4H_9)_2SiC\equiv C-CH=CH_2$	85,18	83,76	+1,42	84,77	+0,41	[32]
$(CH_3)_2Si(C\equiv C-CH=CH_2)_2$	56,49	53,90	+2,59	56,40	+0,09	[32]
$C_6H_5(CH_3)_2SiCH=CH-CH=CH_2$	48,86	47,86	+1,00	49,02	−0,16	[33]
$(C_6H_5)_2CH_3SiCH=CH-CH=CH_2$	53,50	52,49	+1,01	53,53	−0,03	[33]
$(C_2H_5)_2SiCH=CH-CH=CH_2$	58,15	57,12	+1,03	58,04	+0,11	[33]
$Si(C_6H_5)_4$	48,34	48,8	−0,46	48,32	+0,02	[4]
$(n\text{-}C_3H_7)_2Si(C_2H_5)_2$	57,83	58,06	−0,23	57,82	+0,01	[34]
$(n\text{-}C_3H_7)_3SiC_6H_5$	62,55	62,69	−0,14	62,57	−0,02	[34]
$(CH_3)_3SiOH$	26,18	26,19	−0,01	26,21	−0,02	[35]
$(C_6H_5)_3SiOH$	39,78	40,08	−0,3	39,74	+0,04	[35]
$(CH_3)_2Si(n\text{-}C_6H_{13})_2$	48,80	48,80	0,00	48,80	0,00	[36]
$Si(C_6H_5)_4$	85,50	85,84	−0,34	85,52	−0,02	[37]
$H_3SiC_6H_5$	30,97	31,06	−0,09	30,99	−0,02	[36]

corrections for each such radical also has little sense since it is more convenient to calculate MR with the group refractions. It is understood that the table of group refractions may be extended without a limit on the basis of experimental data. However, one should concentrate in the table only those group refractions of radicals whose calculation from bond refractions leads to incorrect or inaccurate values.

However, for the convenience in the use of the table, we placed in it as well some group refractions of radicals which are often encountered and which do not posses an exaltation of MR. The MR for a series of organosilicon compounds, calculated from the bond and the group refractions, are given in Table 5. In case of the use of bond refractions, it is seen in Table 5 that the exaltation of MR for some compounds reaches such large values that the MR of these compounds loses its significance. The use of the value of group refractions proposed by us* totally excludes any unpermissable large deviation of the calculated and the found MR for the compounds indicated in Table 5.

SUMMARY

1. A series of radicals was discovered whose presence in organosilicon compounds is accompanied by an exaltation of molar refraction. Some general points in the chemical structure of these radicals were noted.

2. It was shown that this exaltation of MR is an additive magnitude i.e., one that is directly proportional to the number of radicals having such an exaltation and bound to silicon.

3. The group refractions for 34 radicals connected to a silicon atom were calculated.

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POLYMERIZATION OF STYRENE IN EMULSION UNDER THE INFLUENCE OF THE INITIATING SYSTEM OF CUMENE HYDROPEROXIDE – TRIETHYLENETETRAMINE

S. D. Razumovskii and S. S. Medvedev

The oxidation-reduction methods of initiation of polymerization in aqueous emulsions have received a wide acceptance. As an example of an oxidation-reduction system one may cite that of a hydroperoxide-polyethylene-polyamine, whose initiating action was found to be quite satisfactory for the copolymerization of butadiene with styrene [1]. A number of investigators have studied the reaction between the hydroperoxides and polyamines in aqueous solutions [2-4]. However the literature lacks any data on the reaction of hydroperoxide with amines in hydrocarbon media.

The reaction between benzoyl peroxide and various amines in hydrocarbon media has been studied in detail. The most extensive work in this direction was performed by Gambar'ian and his students [5], Horner and co-workers [6] and Medvedev with F. Grabak [7]. Horner and Medvedev and Grabak conclude on the basis of their experimental data that the reaction between benzoyl peroxide and dimethylaniline goes through a stage of formation of an unstable molecular compound, which decomposes at an appreciable rate, while free radicals are present in the decomposition products. Imoto and Choe [8] propose a probable mechanism of formation of the intermediate molecular compound which is based on the peculiarities of structure of the peroxide. The present work is devoted to the study of the kinetics of reaction of cumene hydroperoxide with triethylenetetramine in an emulsion medium and to the study of the kinetics of emulsion polymerization under the influence of this initiating system.

EXPERIMENTAL

The following were used as the starting materials:

Emulsifier. Mersolat – a mixture of sodium salts of sulfonated paraffins from C_{15} to C_{18} – was used as the emulsifier in the form of paste containing 81% dry matter.

Ethylbenzene. Commercial ethylbenzene was redistilled in nitrogen atmosphere after which it was tested for the presence of peroxidic compounds. The ethylbenzene used in the work was free of peroxidic compounds.

Styrene. The rectified styrene, washed free of inhibitor, was used after having been dried and distilled twice in nitrogen atmosphere.

The description of purification of cumene hydroperoxide (CHP) and triethylenetetramine (TA) was given in our previous paper [4].

Determination of CHP. The determination of CHP in the mixture under analysis was done by the iodometric method. A sample of the emulsion, having a volume of 10 ml, was taken from the reaction flask and was poured into a flask with 5 ml of concentrated hydrochloric acid. 2 ml of saturated solution of potassium iodide was added to this mixture. The liberated iodine was titrated with sodium thiosulfate after 20 minutes of continuous stirring. It was shown by preliminary experiments that the presence of TA does not interfere with the determination of CHP by the iodometric method.

The metering installation and the preparation of mixtures. On Fig. 1 there is shown the metering installation by means of which we prepared the mixtures for the experiments of polymerization under conditions which exclude the presence of even traces of oxygen. The following order of distribution of the components in the

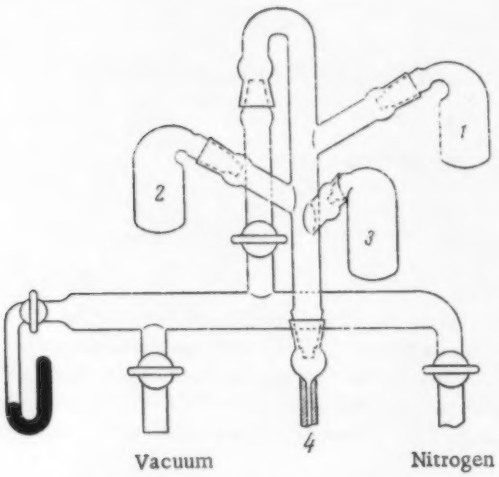

Fig. 1. Metering installation.

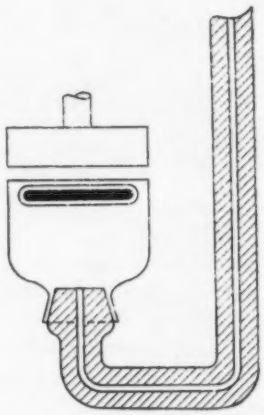

Fig. 2. Dilatometer with stirrer.

apparatus was adopted: vessel 3 contained styrene and CHP; vessel 2 – the solution of emulsifier, TA and iron salts; vessel 1 – only water. The removal of oxygen from the components of the mixture was done as follows: at first the liquids in all three vessels were frozen and vacuum was established in the system at 1-3 mm of mercury, after which the liquids were carefully thawed; the dissolved air was thus expelled from them, after which the apparatus was filled with oxygen-free nitrogen. This operation was repeated three times after which vacuum was again established in the system and the liquids were mixed in dilatometer 4 in a definite order.

Dilatometer. The dilatometer is shown in Fig. 2. The stirring in it was accomplished by means of a magnetic stirrer. The working location of this stirrer at the upper wall of the dilatometer is original. This location permitted us to attain a very energetic stirring of the emulsion in the dilatometer, this being necessary for polymerization which proceeds at a high rate. It was shown by special experiments that the rate of polymerization is independent of the rate of stirring if the rotational rate of the stirrer is above 250 RPM. In the systematic runs the rate of stirrer rotation was equal to 350 RPM. We judged the degree polymerization by the lowering of the liquid in the capillary. The degree of polymerization was calculated from the densities of styrene and polystyrene known from the literature. The data from the calculations were checked by the determination of polystyrene yield. The deviation did not exceed 2% for degree of polymerization of 47%.

Reaction vessel. The reaction vessel for the study of kinetics of reaction of CHP and TA in emulsion was described in an earlier paper [4].

1. Reaction of CHP and TA in Soap Solutions and Emulsions

The study of the kinetics of reaction between CHP and TA was done in ethylbenzene emulsion. Ethylbenzene was selected as the substance which reproduces most of the properties of styrene while being incapable of polymerizing. The emulsifier concentration was maintained at 24 g per liter invariably in all experiments. The ratio of the hydrocarbon and the aqueous phases of the emulsion was 1:3. Since the concentrations of the reacting components in this reaction were unknown, we used for all the following calculations the values of concentration calculated on the total volume of the system. In Figs. 3 and 4 are given the relationships of the reaction rate with the total concentration of iron in the soap solution and emulsion. The study of this relationship leads to the conclusion that the rate of the CHP-TA reaction in soap solution and emulsion is directly proportional to the iron concentration in the system. It is evident from these graphs that a significant reaction rate exists even without the

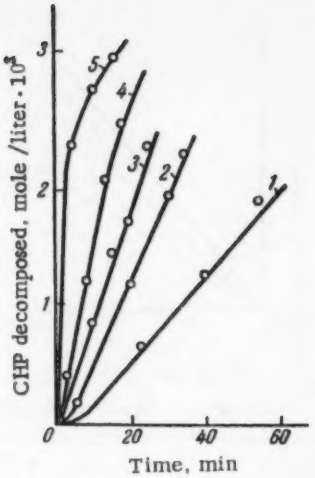

Fig. 3. Dependence of the reaction rate of TA−CHP in soap solutions on the concentration of iron with: TA $1.07 \cdot 10^{-2}$ mole/liter; CHP $0.34 \cdot 10^{-2}$ mole/liter; t = 20°; $Fe_2(SO_4)_3$; 1) 0; 2) $0.426 \cdot 10^{-5}$; 3) $0.85 \cdot 10^{-5}$; 4) $1.75 \cdot 10^{-5}$; 5) $3.5 \cdot 10^{-5}$ mole/liter.

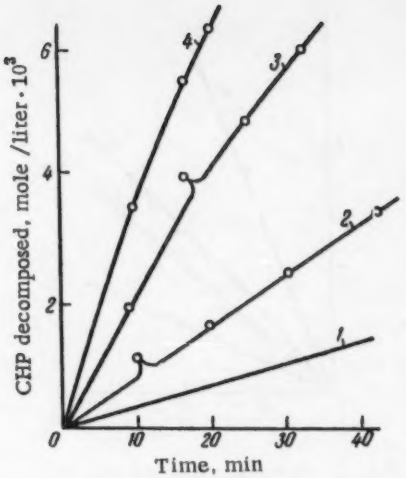

Fig. 4. Dependence of the rate of reaction of TA−CHP in ethylbenzene emulsions on the concentration of iron at: TA $2.18 \cdot 10^{-2}$ mole/liter; CHP $0.84 \cdot 10^{-2}$ mole/liter; t = 18°; $Fe_2(SO_4)_3$; 1) 0 + ethylenediaminetetracetic acid as the sodium salt; 2) 0; 3) $4.26 \cdot 10^{-6}$; 4) $8.50 \cdot 10^{-6}$ mole/liter.

addition of iron salts. Evidently traces of iron in the emulsifier cause the observed reaction. An analysis showed that the original emulsifier contained $0.6 \cdot 10^{-6}$ moles/g of iron calculated as $Fe_2(SO_4)_3$. A drop of the catalytic activity of dilute solutions of iron salts in storage was observed in the study of the CHP−TA reaction in the presence of iron salts both in aqueous solutions [4] and in emulsions. Solutions of iron salts having the greatest activity were used for our experiments. Experimental data on the dependence of the rate of reaction of CHP−TA on the total concentration of CHP are given in Figs. 5, 6 and 7: for soap solution (Fig. 5), soap solution saturated with ethylbenzene (Fig. 6) and ethylbenzene emulsion (Fig. 7). The dependence of the reaction rate on the overall concentration of CHP may be expressed in the form of an index function: $w_p = k[CHP]^a$. The value of index a, may be calculated from the data of Figs. 5, 6 and 7. The appropriate calculations led to the conclusion that in transition from soap solutions to soap solutions saturated with ethylbenzene and, further, to ethylbenzene emulsions, there occurs a gradual decrease of the power index a, which assumes successively the values of 0.8, 0.56 and 0.4. This difference in the value of the index is evidently connected with the variation of distribution of CHP among the phases of the system in transition from the soap solution to the emulsions (Fig. 8).

The data on the study of the effect of TA concentration on the reaction rate in emulsion are shown in Fig. 9. The dependence of the reaction rate on the initial TA concentration in the system may be expressed by the power index function: $w_p = k[TA]^{0.2}$. A study of the dependence of the reaction of CHP−TA in emulsion on the temperature allowed us to determine the value of the apparent activation energy of the summary reaction in emulsion, which turned out to be 16.1 kilocalories per mole. Some experiments on the study of the reaction of benzoyl peroxide with amino compounds in ethylebenzene in the absence of iron were set up. These showed that benzoyl peroxide reacts energetically with both dimethylaniline and with TA.

CHP does not react with either dimethylaniline or TA under these conditions. An energetic reaction between CHP and TA is observed in ethylbenzene in the presence of iron naphthenate.

2. Polymerization of Styrene in Emulsions

The effect of alterations on the initial concentrations of iron, CHP and TA on the rate of polymerization of styrene in emulsion was studied (Figs. 9, 10 and 11). It is evident from Fig. 9 that polymerization of styrene

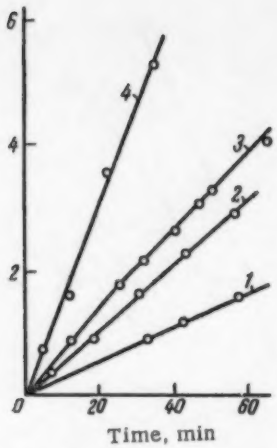

Fig. 5. Dependence of the rate of reaction of TA–CHP in soap solutions on the concentration of CHP with: TA $1.96 \cdot 10^{-2}$ mole/liter; $Fe_2(SO_4)_3$0; t = 20°; CHP: 1) $0.24 \cdot 10^{-2}$; 2) $0.49 \cdot 10^{-2}$; 3) $0.84 \cdot 10^{-2}$; 4) $1.70 \cdot 10^{-2}$ mole/liter.

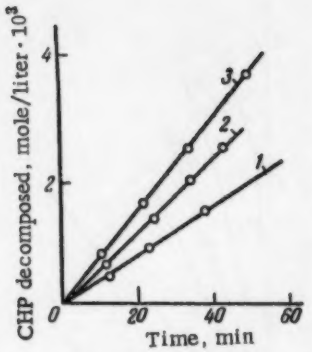

Fig. 6. Dependence of the rate of reaction of CHP–TA in soap solutions saturated with ethylbenzene on CHP concentration with: TA $1.96 \cdot 10^{-2}$ mole/liter; $Fe_2(SO_4)_3$0; t = 20°; CHP: 1) $0.24 \cdot 10^{-2}$; 2) $0.49 \cdot 10^{-2}$; 3) $0.84 \cdot 10^{-2}$ mole/liter.

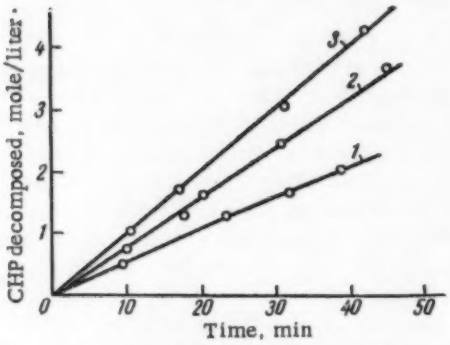

Fig.7. The dependence of the reaction rate of CHP–TA in emulsion on the CHP concentration with: TA $2.18 \cdot 10^{-2}$ mole/liter; $Fe_2(SO_4)_3$0; t = 18°; CHP: 1) $0.43 \cdot 10^{-2}$; 2) $0.84 \cdot 10^{-2}$; 3) $1.70 \cdot 10^{-2}$ mole/liter.

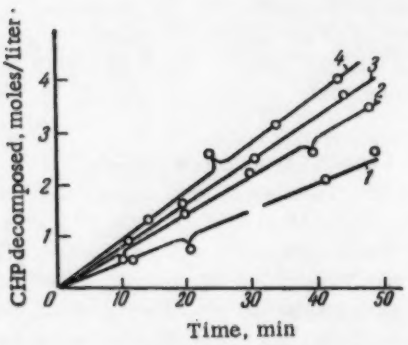

Fig. 8. The dependence of the reaction rate of CHP–TA in emulsion on the concentration of TA with: CHP $0.84 \cdot 10^{-2}$ mole/liter; $Fe_2(SO_4)_3$0; t = 18°; TA: 1) $0.49 \cdot 10^{-2}$; 2) $1.24 \cdot 10^{-2}$; 3) $2.18 \cdot 10^{-2}$; 4) $4.36 \cdot 10^{-2}$ mole /liter.

proceeds at an appreciable rate without added iron salts, which fact is evidently connected with the presence of traces of iron in the emulsifier. The polymerization rate increases upon introduction of iron salts into the system, but at iron concentrations above $3.6 \cdot 10^{-5}$ mole/liter the rate of the process no longer depends on the amount of added iron up to $1 \cdot 10^{-4}$ mole /liter cauculated as $Fe_2(SO_4)_3$. With further increase of iron concentration, the rate of reaction of CHP–TA rises to such a degree that with even low degrees of polymerization an exhaustion of the initiating system takes place (Fig. 9, curve 5). A new addition of CHP to the system brings about the previous rate of polymerization. A comparison of the action of ferrous and ferric salts showed that if these are taken in equivalent amounts, the rate of polymerization is not changed by such substitution.

The data on the dependence of the rate of styrene polymerization on concentrations of CHP and TA in the presence and absence of iron are graphically given in Figs. 10 and 11. The rate of polymerization in all cases rapidly reached its maximum value after which it no longer depended on the concentrations of CHP and TA. Thus, the polymerization rate does not depend on the rate of reaction of CHP with TA in emulsion over a wide interval

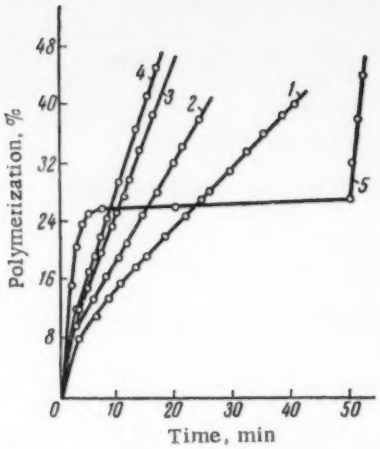

Fig. 9. Dependence of the rate of polymerization on iron salts with: TA $2.18 \cdot 10^{-2}$ mole /liter; CHP $1.5 \cdot 10^{-2}$ mole/liter; t = 5°; $Fe_2(SO_4)_3$: 1) 0; 2) $7.6 \cdot 10^{-6}$; 3) $3.6 \cdot 10^{-5}$-$7.6 \cdot 10^{-5}$; 4) $Fe_4(P_2O_7)_3$ $1.0 \cdot 10^{-2}$ mole /liter; TA = 0; 5) $76 \cdot 10^{-5}$ mole / liter.

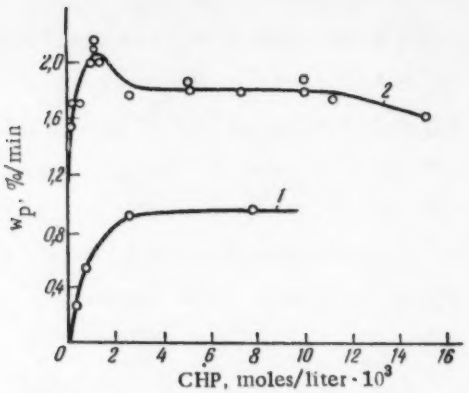

Fig. 10. Dependence of initial polymerization rate w_p on the concentration of CHP with: TA $2.65 \cdot 10^{-2}$ mole/liter; t = 5°; $Fe_2(SO_4)_3$: 1) 0; 2) $5.32 \cdot 10^{-5}$ mole /liter.

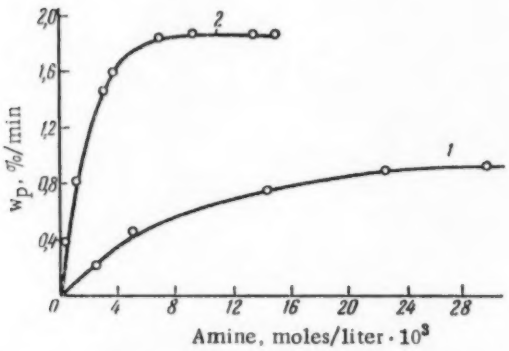

Fig. 11. Effect of TA on initial polymerization rate with: CHP $0.84 \cdot 10^{-2}$ mole /liter; t = 5°; $Fe_2(SO_4)_3$: 1) 0; 2) $5.32 \cdot 10^{-5}$ mole /liter.

of concentrations of all the components of the initiating system. This forces us to suppose that the effectiveness of initiation for the CHP–TA system is quite low.

It was indicated above that in the reaction of benzoyl peroxide with amines it is most probable that the first stage of the reaction is the formation of an unstable molecular complex, which originates owing to the structural peculiarities of both the amine and of the peroxide. The structure of hydroperoxides, specifically CHP, differs from that of benzoyl peroxide and, evidently, owing to this fact the formation of unstable molecular complexes between amines and hydroperoxides is blocked. Therefore, CHP does not react with TA and dimethylaniline in ethylbenzene. The reaction occurs only in the presence of iron. The possible mechanism of action of iron salts was given by us in a previous paper [4]. The initiation of the polymerization processes by the system of benzoyl peroxide-dimethylaniline results from the formation of the molecular complex compound [7, 8]. This is not observed in case of initiation by the CHP–TA system in emulsion (Fig. 9, curve 5) in which polymerization stops when CHP disappears from the system and begins again after the addition of the latter to the system. This fact also confirms the reaction mechanism proposed earlier [4].

SUMMARY

1. The kinetics of reaction of cumene hydroperoxide with triethylenetetramine in soap solutions and emulsions was studied. A dependence of the reaction rate on the concentration of the reaction components was established and some suppositions were made about the reaction mechanism.

2. The kinetics of polymerization of styrene in emulsion under the influence of the cumene-hydroperoxide–triethylenetetramine system was studied. It was established that the effectiveness of the initiating action of this system is quite small.

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REACTIONS OF TRIAZENES WITH DIENOLS AND ACIDS IN ANHYDROUS HYDROCARBON MEDIA

E. I. Tiniakova, V. Ia. Bogomol'nyi and T. G. Zhuravleva

It has been established by recent work that the decomposition of alkaryl triazenes in aqueous media is catalytically accelerated by the influence of dienols, acids and other substances of acidic nature [1, 2]. The decomposition of triazenes in hydrocarbon media in the absence of water is also strongly accelerated by the presence of acids, but the process does not proceed with a catalytic mechanism since the reaction is accompanied by formation of esters [2, 3]. It appeared useful to study the possibility of applying the latter reaction to the quantitative estimation of carboxyl groups in organic compounds. There was also material interest in the study of the reaction of triazenes with dienols in anhydrous media because of the possibility of using it for alkylation or arylation of dienolic groups. The present study is devoted to these two points.

The possibility of a volumetric determination of the content of carboxyl groups by the volume of evolved nitrogen was first confirmed with examples of benzoic and methacrylic acids. The reaction was run at 20-60° with various ratios of the acid and methylphenyltriazene in dry toluene solution. The experimental data, given in Table 1, show that the amount of decomposed methylphenyltriazene is equivalent to the amount of acid introduced.

TABLE 1

Determination of Benzoic and Methacrylic Acids in the Reaction with Methylphenyltriazene in Toluene Solution

Acid	Sample of acid (g)/ /10 ml of toluene	Sample of methyl-phenyltri-azene, g	Temp. in °C	Vol. of N evolved, ml (at STP)	Evolved N, in % of theoret.
Benzoic	0,0316	0,10	20	5,8	100
»	0,0341	0,10	20	6,2	100
»	0,0517	0,20	60	9,8	103
»	0,0630	0,15	20	12,2	105
»	0,0715	0,17	22	13,4	102
»	0,0765	0,25	25	14,7	105
»	0,0837	0,25	25	15,6	101
»	0,0936	0,25	20	18,4	106
»	0,1148	0,25	40	22,2	105
»	0,2061	0,35	20	38,8	102
Methacrylic	0,1133	0,4	20	30,5	103
»	0,0817	0,4	25	21,9	102

The error of the determination was +3% to +5% of the introduced amount which fact permitted us to use this method for the determination of the content of carboxylic groups in some polymers, as for example copolymers of dienes with small amounts of acrylic acids. The polymer in this case was dissolved in toluene. After the removal of traces of water by distillation in the form of an azeotrope with toluene and after cooling the solution, methylphenyltriazene was introduced into the latter and the system was connected to a gas burette. The evolution of

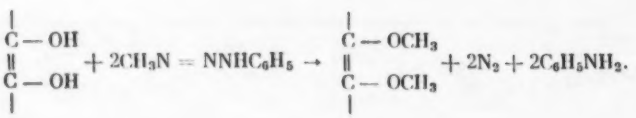
nitrogen ended at 60° within 2-3 hours. The resulting data, shown in Table 2, indicate a satisfactory reproducibility of the results in parallel runs.

TABLE 2

Determination of the Content of Carboxyl Groups in Polymers by the Reaction with Methylphenyltriazene

Polymer type	Content of methacrylic acid in %	
	in polymerizing mixture	in the polymer
Copolymer of butadiene with styrene and methacrylic acid SKS-10-1	1,1	1,03 1,04 1,20 1,17
Copolymer of butadiene with styrene and methacrylic acid SKS-30-1	1,2	1,28 1,34 1,46 1,25 1,36 1,27 1,36 1,37
	1,5	1,64 1,68
	2,0	2,42
	4,0	4,62
	5,0	6,78 6,18
Copolymer of butadiene with methacrylic acid	4,0	4,03
Copolymer of isoprene with methacrylic acid	4,0	3,91 4,05

One could assume, by analogy with the action of acids, that dienols would also accelerate the decomposition of the triazenes and the reaction would be accompanied by a disappearance of the dienolic groups in accord with the following over-all equation:



The evolving gas should consist of pure nitrogen in this case. As it is known [4], the gas in case of thermal decomposition of triazenes in hydrocarbon medium contains considerable amounts of methane, owing to the reaction: $CH_3^{\cdot} + AH \rightarrow CH_4 + A^{\cdot}$, where AH is the solvent, dienol or some other compound. We used ascorbic acid, dihydroxymaleic acid and its diethyl ester as the dienols, while methylphenyltriazene and diazoaminobenzene were used as the triazenes. The reaction was run at the temperature of 60-70° in dry toluene solution.* The amount of the triazene comprised 5-10 moles per 1 mole of the dienol.

The kinetics of gas evolution during the decomposition of methylphenyltriazenes in the present of dihydroxymaleic acid is shown in Fig. 1. The gas was pure nitrogen according to the analytical data. The amount of the evolved gas amounted to 4 moles per 1 mole of acid in all experiments regardless of the size of the excess of triazene, this proportion being in correspondence with the participation of two carboxyl and two dienolic groups in the reaction. The analysis of the product after termination of nitrogen evolution showed the absence of free carboxyl or dienolic groups. It should be noted that in the beginning of the reaction the system is heterogeneous owing to the insolubility of dihydroxymaleic acid in toluene. The reaction mixture became homogeneous after a

*The thermal decomposition of triazenes does not occur under these conditions.

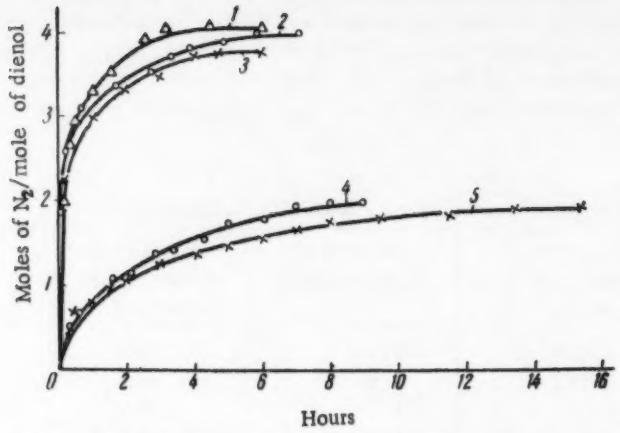


Fig. 1. Kinetics of nitrogen evolution in decomposition of methylphenyltriazene in toluene solution at 70° in the presence of dihydroxymaleic acid (1, 2, 3) and diethyl dihydroxymaleate (4, 5). The ratio of dienol to methylphenyltriazene in moles: 1) 1:10; 2) 1:5; 3) 1:8; 4) 1:8; 5) 1:5; dienol concentration: 1) 0.0131; 2) 0.097; 3) 0.0178; 4) 0.0270; 5) 0.0396 mole/liter.

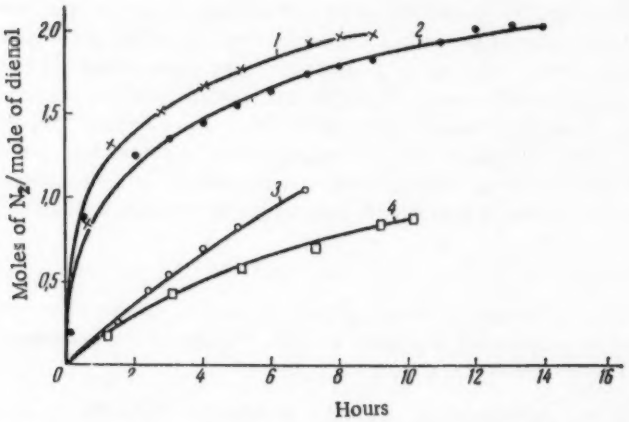


Fig. 2. Kinetics of nitrogen evolution in decomposition of diazoaminobenzene in the presence of diethyl dihydroxymaleate (1, 2) and of methylphenyltriazene in the presence of ascorbic acid (3, 4). The dienol:triazene ratio in moles: 1) 1:8; 2) 1:5; 3) 1:5; 4) 1:4; dienol concentration: 1) 0.0393; 2) 0.0337; 3) 0.0435; 4) 0.0476 moles/liter.

brief interval of time owing to the formation of the soluble dimethyl ester. This moment corresponds to the evolution of approximately 50% of total nitrogen and to an inflection in the kinetic curve. The retardation of the rate of nitrogen evolution is evidently explained by the lesser rate of alkylation of the enolic groups in comparison with the carboxyls.

The participation of the dienolic groups of dihydroxymaleic acid in the reaction is confirmed by the data on the decomposition of methylphenyltriazene in the presence of diethyl dihydroxymaleate (Fig. 1, curves 4, 5) which contains only the dienolic grouping. The reaction rate in this case was lower than with dihydroxymaleic

acid. The amount of evolved nitrogen was equal to 2 moles per 1 mole of the ester. No free dienolic groups were found in the reaction products. Dihydroxymaleic acid and its ester cause the decomposition of a purely aromatic triazene – diazoaminobenzene under the same conditions; their action may be illustrated by the example of decomposition of diazoaminobenzene in the presence of diethyl dihydroxymaleate (Fig. 2). The reaction is accompanied by evolution of 2 moles of nitrogen per 1 mole of the ester and by consumption of the dienol.* Similar

TABLE 3

Decomposition of Methylphenyltriazene in the Presence of Ascorbic Acid

Expt. No.	Concentration of ascorbic acid in moles/liter	Molar ratio of dienol : triazene	Amount of evolved nitrogen in % of theoretical	Amount of unreacted dienolic groups in % of theoretical
1	0.0257	1:4	15.4	73.5
2	0.0362	1:6	95.0	10.0
3	0.0177	1:5	33.0	47.5
4	0.0340	1:4	19.9	69.0

results were obtained in the study of the decomposition of triazenes in the presence of ascorbic acid (Fig. 2). In this case also the degree of decomposition of the triazene corresponds to the amount of consumed dienolic groups (Table 3).

EXPERIMENTAL

Purified toluene, distilled from metallic sodium, was used in all experiments. Methylphenyltriazene, dihydroxymaleic acid and its ester were synthesized by us according to appropriate methods [5, 7]. The experiments on the determination of the content of the carboxyl groups, as well as on the decomposition of triazenes in the presence of dihydroxymaleic ester, were run in Tserevitinov-type flasks connected to a gas burette. In the study of the decomposition of triazenes in the presence of dihydroxymaleic acid, the experiments were run in a three-necked flask with a stirrer, a dropping funnel and a connection to a gas burette. The process was completed after the gas volume no longer changed. The evolved gas was subjected to a complete gas analysis. The determination of the dienol groups was made in the reaction mixture after completion of the reaction, using Bertrand's method [8] or iodometrically; the free carboxyl groups were determined by titration with alkali.

SUMMARY

1. It was shown that dihydroxymaleic acid and its diethyl ester as well as ascorbic acid accelerate the decomposition of triazenes in anhydrous hydrocarbon media. The reaction is accompanied by evolution of nitrogen and by alkylation (arylation) of carboxyl and dienolic groups.

2. It was shown that the decomposition reaction of triazenes under the influence of acids may be used for a volumetric quantitative method of determination of carboxyl groups in hydrocarbon media, specifically in polymers.

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* A certain amount of carbon dioxide is present along with nitrogen in the gas evolved in the decomposition of diazoaminobenzene in the presence of dihydroxymaleic acid; this is evidently explained by decarboxylation of the resulting tetraphenyl ester of dihydroxymaleic acid.

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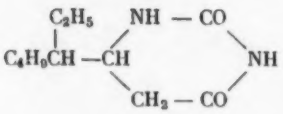
CONCERNING SOME TRANSFORMATION PRODUCTS OF DIASTEREOISOMERIC γ-ETHYL-β-N-CARBETHOXYAMINOCAPRYLIC ACIDS

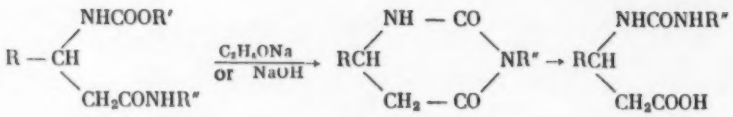
V. K. Zvorykina and O. Ia. Neiland

Two diastereoisomers of γ-ethyl-β-aminocaprylic acid, $C_4H_9CH(C_2H_5)CH(NH_2)CH_2COOH$, provisionally named isomers A_1 and A_2, were prepared in our previous studies with Rodionov, along with a series of their derivatives and transformation products [1, 2, 3]. It was discovered in the biological tests of some of them that γ-ethyl-β-ureidocaprylic acids, $C_4H_9CH(C_2H_5)CH(NHCONH_2)CH_2COOH$ (predominantly isomer A_2) have bacteriostatic action against acid-resistant bacteria and pathogenic fungi, while 4-(1-ethylpentyl)-2,6-dioxohexahydropyrimidine:



(isomer A_2) turned out to be active in vitro against the grippe viruses [2]. Isomers A_1 and A_2 of γ-ethyl-β-ureidocaprylic acid and 4-(1-ethylpentyl)-2,6-dioxohexahydropyrimidines, which are rather close in their chemical reactions, showed a considerably greater difference in their biological properties.

Therefore, in a further study it was interesting to conduct a parallel comparison of the chemical and the biological properties of compounds of this type in which the molecular configuration is retained while substituents are introduced into the functional groups. For this purpose we prepared diastereoisomeric (A_1 and A_2) γ-ethyl-β-(ω-phenylureido)caprylic acids, γ-ethyl-β-semicarbazidocaprylic acids and 1-phenyl-4-(1-ethylpentyl)-2,6-dioxohexahydropyrimidines. For their synthesis we used the reaction that had been discovered by Rodionov and Zvorykina for the amides of N-carbalkoxy derivatives of β-amino acids (a) [4], and which was later extended to the hydrazides (b) [5] and substituted amides [6]; this reaction in a general form may be expressed by the following scheme:



a) R" = H ureido acid;
b) R" = NH_2 semicarbazido acid;
c) R" = alkyl or aryl; β-(ω-alkyl or arylureido) acid.

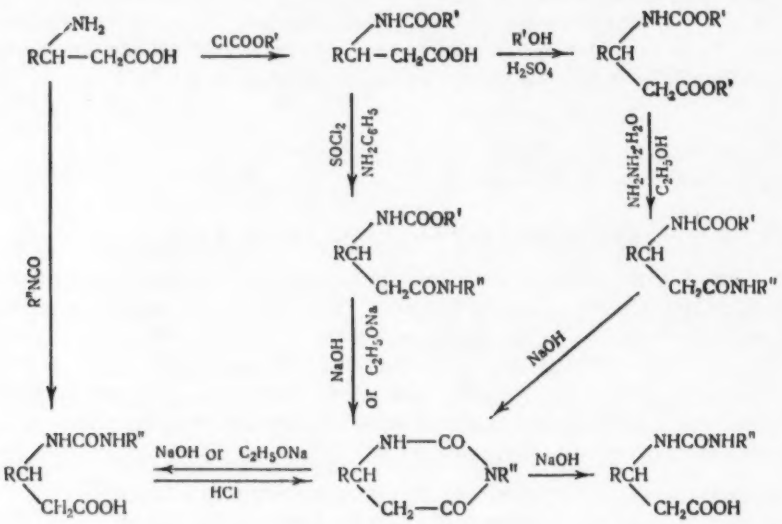
The intermediate product of this reaction – substituted 2,6-dioxohexahydropyrimidine – may be isolated if one runs the experiment in the cold with an alcoholic solution of sodium alcoholate [4].

We failed to isolate 1-phenyl-4-(1-ethylpentyl)-2,6-dioxohexahydropyrimidines in case of the reaction of the anilide of γ-ethyl-β-N-carbethoxyaminocaprylic acid. Evidently the presence of the phenyl radical hindered the reaction: the starting material was recovered in the reaction in the cold with sodium alcoholate, while on heating an opening of the pyrimidine ring occurred with formation of γ-ethyl-β-(ω-phenylureido)caprylic acid;

its yield (of isomer A_1 as well as of isomer A_2) was about 80%.

The isomeric 1-phenyl-4-(1-ethylpentyl)-2,6-dioxohexahydropyrimidines were prepared by us by ring closure of γ-ethyl-β-(ω-phenylureido)caprylic acids (A_1 and A_2) by heating them with hydrochloric acid under conditions described by Rodionov and Viazkova [7].

The isomeric γ-ethyl-β-(ω-phenylureido)caprylic acids were also prepared for yield comparison, besides the above-described reaction (scheme 1), by the method of Longfield and Stieglitz [8], by the action of phenylisocyanate on γ-ethyl-β-aminocaprylic acids [3] and by hydrolysis of 1-phenyl-4-(1-ethylpentyl)-2,6-dioxohexahydropyrimidines [4]. The entire sequence of the transformations run by us may be shown in the following scheme:



c) γ-ethyl-β-(ω-phenylureido)caprylic acid

d) 1-phenyl (or amino) 4-(1-ethylpentyl)-2,6-dioxohexahydropyrimidine

b) γ-ethyl-β-semicarbazido acid

c or b) R = $C_4H_9CH(C_2H_5)$—, R' = C_2H_5; c) R" = NH_2; b) R" = C_6H_5

EXPERIMENTAL

γ-Ethyl-β-aminocaprylic acids (isomers A_1 and A_2) and their carbethoxy derivatives were prepared under conditions described by Rodionov and Zvorykina [1].

Preparation of Ethyl Esters of γ-Ethyl-β-N-carbethoxyaminocaprylic Acids A_1 and A_2

6.3 g of the N-carbethoxy derivative of γ-ethyl-β-aminocaprylic acid (isomer A_1) was refluxed for 8 hours on a stream bath with 60 ml of ethyl alcohol and 5 ml of concentrated sulfuric acid. The residue after the distillation of alcohol was diluted with water and extracted with ether. The ether extract was dried over sodium sulfate, ether was distilled and the residue was vacuum distilled. 4.4 g of ethyl ester of γ-ethyl-β-N-carbethoxyaminocaprylic acid (A_1) with b.p. 179-182° (12 mm) was obtained for a 63% yield.

5.2 g of the ethyl ester of γ-ethyl-β-N-carbethoxyaminocaprylic acid (A_2) with b.p. 176-178° (12 mm) (57%) was obtained under the same conditions from 8.2 g of carbethoxy derivative (A_2).

Preparation of Hydrazides of γ-Ethyl-β-N-carbethoxyaminocaprylic Acids (A_1 and A_2)

4.4 g of the ethyl ester of γ-ethyl-β-N-carbethoxyaminocaprylic acid (isomer A_1) was refluxed for 18 hours with 2.5 g of hydrazine hydrate in 15 ml of ethyl alcohol on a steam bath. The alcohol was distilled and the residue was triturated with 20 ml of water, filtered and recrystallized from 50% alcohol. 3.25 g of isomer A_1 of γ-ethyl-β-N-carbethoxyaminocaprylic acid hydrazide with m.p. 112° was obtained. The melting point rose to 115° (colorless needles) and failed to change further after repeated recrystallization and drying at 70°. Additional 0.7 g with m.p. 105-107° was obtained from the mother liquor.

Under the same conditions, 3.7 g (71%) of γ-ethyl-β-N-carbethoxyaminocaprylic acid hydrazide (isomer A_2) with m.p. 87-92° was obtained from 5.2 g of the ethyl ester of γ-ethyl-β-N-carbethoxyaminocaprylic acid (isomer A_2) and 2.7 g of hydrazine hydrate; the melting point rose to 94-95° and failed to change further after recrystallization from 50% alcohol; the product formed colorless needles.

Found for isomer A_1 %: N 15.17; 15.30
Found for isomer A_2 %: N 15.34; 15.41
$C_{13}H_{27}N_3O_3$. Calculated %: N 15.38.

Preparation of γ-Ethyl-β-Semicarbazidocaprylic Acids A_1 and A_2.

1.7 g of γ-ethyl-β-N-carbethoxyaminocaprylic acid hydrazide (isomer A_1) was heated for 5 minutes at reflux with 13 ml of 10% solution of sodium hydroxide. The solution was cooled and acidified with acetic acid. The resulting precipitate was filtered off, washed with ether and dried at 70°. 1.5 g of γ-ethyl-β-semicarbazidocaprylic acid (A_1) with m.p. 120° was obtained (about 92%). The melting point rose to 123° (colorless needles) after recrystallization from alcohol. Under the same conditions 1.7 g of hydrazide A_2 yielded 0.5 g of γ-ethyl-β-semicarbazidocaprylic acid (A_2) with m.p. 119° (colorless needles) while 0.3 g with m.p. 110-112° was obtained further from the mother liquor for a total yield of 53%.

Found for isomer A_1 %: C 54.39; 54.43; H 9.31; 9.43; N 17.37; 17.35
Found for isomer A_2 %: C 54.39; 54.15; H 9.31; 9.34; N 17.51; 17.48
$C_{11}H_{23}N_3O_3$. Calculated %: C 53.87; H 9.38; N 17.14

Preparation of γ-Ethyl-β-N-Carbethoxyaminocaprylic Acid Anilides A_1 and A_2

6.1 g of isomer A_1 of carbethoxyaminocaprylic acid was heated for 3 hours at 40-45° with 4 ml of thionyl chloride. The excess of the latter was vacuum distilled and the residue was dissolved in 150 ml of absolute ether and to this solution 5 ml of aniline was added dropwise with cooling. Ether was distilled, the residue was treated with 100 ml of 6% hydrochloric acid, filtered and washed with hot water. 53 g of γ-ethyl-β-N-carbethoxyaminocaprylic acid anilide (isomer A_1) with m.p. 133° (fine colorless needles) was obtained after recrystallization from alcohol and drying at 70-80°.

Under the same conditions 5 g of the carbethoxy derivative of isomer A_2 we obtained 4 g (63%) of β-N-carbethoxyaminocaprylic acid anilide (isomer A_2) with m.p. 114° (colorless needles from 50% alcohol).

Found for isomer A_1 %: N 8.64; 8.51
Found for isomer A_2 %: N 8.62; 8.48
$C_{18}H_{30}N_2O_3$. Calculated %: N 8.38

Preparation of γ-Ethyl-β-(ω-Phenylureido)-Caprylic Acids A_1 and A_2.

1) From anilides with NaOH in 50% alcohol. 1.0 g of γ-ethyl-β-N-carbethoxyaminocaprylic acid anilide (A_1) was refluxed for 4 hours with 5 ml of 20% sodium hydroxide solution and 5 ml of ethyl alcohol. The solution was diluted with 50 ml of water, heated to boiling, filtered and acidified to Congo red. The resulting precipitate was filtered off and recrystallized from alcohol. 0.48 g (52%) of γ-ethyl-β-(ω-phenylureido)-caprylic acid with m.p. 173° was isolated. The melting point rose to 175° (colorless needles) after repeated recrystallization from alcohol.

Under the same conditions 1 g of the anilide (isomer A_2) gave 0.4 g of γ-ethyl-β-(ω-phenylureido)caprylic acid with m.p. 145° (A_2) (fine colorless needles from 25% alcohol) and 0.16 g of unreacted anilide. The yield based on reacted material was 51%.

2) From anilides with sodium alcoholate. 0.5 g of γ-ethyl-β-N-carbethoxyaminocaprylic acid anilide (A_1) was refluxed for two hours with 5 ml of 10% sodium alcoholate solution. The solution was filtered after dilution with water, after which it was acidified to Congo red. The resulting precipitate was filtered off, washed with water and dried at 100°. 0.35 g (79%) of γ-ethyl-β-(ω-phenylureido)caprylic acid (A_1) with m.p. 174° was isolated. The mixed melting point with the A_1 sample from the preceding experiment was 175°.

Under the same conditions 0.9 g of the anilide A_2 gave 0.66 g (80%) of γ-ethyl-β-(ω-phenylureido) caprylic acid isomer A_2 with m.p. 138°. The melting point rose to 144° after recrystallization from alcohol. The mixed melting point with the A_2 sample obtained in the preceding experiment was 145°.

Found for isomer A_1 %: N 9.01; 9.03
Found for isomer A_2 %: N 9.18; 9.19
$C_{17}H_{21}N_2O_2$. Calculated %: N 9.11

3) From γ-ethyl-β-aminocaprylic acids (A_1 and A_2) and phenylisocyanate. 1.3 g of phenylisocyanate was added dropwise, with cooling with ice and stirring, to a solution of 1.9 g of γ-ethyl-β-aminocaprylic acid A_1 in 20 ml of 2.5% sodium hydroxide solution. The stirring continued for one more hour at room temperature after which 50 ml of water was added and the mixture was heated to boiling. The cooled solution was filtered and acidified to Congo red. The resulting precipitate was filtered off, recrystallized from alcohol and dried at 100°. 1.1 g of the product was isolated; m.p. 175°; 0.3 g was also obtained in addition from the mother liquor (m.p. 173°). The total yield was 1.4 g (43%). The mixed melting point with a sample of A_1 from experiment 1) gave no depression.

Under the same conditions 2.9 g of the amino acid (isomer A_2) gave 3 g of γ-ethyl-β-(ω-phenylureido-caprylic acid (isomer A_2) with m.p. 145°; yield – 64% The mixed melting point with a sample from experiment 1) was 145°.

4) From 1-phenyl-4-(1-ethylpentyl)-2,6-dioxohexahydropyrimidine. 0.05 g of 1-phenyl-4-(1-ethylpentyl)-2,6-dioxohexahydropyrimidine A_1 was refluxed for two hours with 2 ml of 10% sodium hydroxide solution and 2 ml of ethyl alcohol. Four ml of water was added after the heating; the solution was filtered and acidified. The precipitate was filtered off; washed with water and dried at 100°. 0.03 g of γ-ethyl-β-(ω-phenylureido)-acid A_1 with m.p. 175° was isolated. The mixed melting point with the A_1 sample from experiment 1) was unchanged.

Preparation of 1-Phenyl-4-(1'-ethylpentyl)-2,6-dioxohexahydropyrimidines A_1 and A_2

0.8 g of γ-ethyl-β-(ω-phenylureido)caprylic acid (A_1) was refluxed for two hours with 15 ml of 17% hydrochloric acid and 5 ml of glacial acetic acid. Fifteen ml of water was added after the heating. The resulting precipitate was filtered off after one hour and was treated with 10% sodium bicarbonate solution while being heated to 60-65°. The undissolved product was filtered off after cooling, washed with water, recrystallized from alcohol and dried at 80°. 0.36 g (47%) of 1-phenyl-4-(1-ethylpenthyl)-2,6-dioxohexahydropyrimidine with m.p. 140° (colorless prisms) was isolated.

Under the same conditions 0.35 g of isomer A_2 of γ-ethyl-β-(ω-phenylureido)-caprylic acid after being boiled for five hours with 3 ml of 17% hydrochloric acid and 3 ml of glacial acetic acid gave 0.14 g of 1-phenyl-4-(1-ethylpentyl)-2,6-dioxohexahydropyrimidine A_2 with m.p. 133° (fine colorless needles from alcohol).

Found for isomer A_1 %: N 9.982; 9.821
Found for isomer A_2 %: N 9.92; 9.91
$C_{17}H_{24}N_2O_2$. Calculated %: N 9.72

SUMMARY

The following previously undescribed derivatives were synthesized for the two diastereoisomeric γ-ethyl-β-aminocaprylic acids (A_1 and A_2): ethyl esters of N-carbethoxy derivatives (A_1 and A_2); hydrazides of N-carbethoxy derivatives (A_1 and A_2); anilides of N-carbethoxy derivatives (A_1 and A_2) and the products of their

transformations: γ-ethyl-β-(ω-phenylureido)caprylic acids (A_1 and A_2), γ-ethyl-β-semicarbazidocaprylic acids (A_1 and A_2) and 1-phenyl-4-(1-ethylpentyl)-2,6-dioxohexahydropyrimidines (A_1 and A_2).

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*Original Russian pagination. See C. B. Translation.

SYNTHESIS OF SULFUR-CONTAINING SUBSTANCES BASED ON VINYL ETHERS AND ACETYLENE

16. CONCERNING THE MOBILITY OF THE β-ALKOXY GROUPS IN ETHYL ALKYL AND ARYL SULFIDES

E. N. Prilezhaeva and M. F. Shostakovskii

The mobility of substituents in the β-position, in respect to the sulfur atom, as displayed in the number of their nucleophilic substitution reactions, is generally known. A very large number of publications* has been devoted to hydrolysis reactions of β-chloro- and bromoethyl alkyl (aryl) sulfides and yperite [1], to the substitution of the halogen atom in these compounds by other atoms [2], as well as to the hydrochlorination reactions of β-hydroxyethyl alkyl (aryl) sulfides [3]. It is possible to assert on the basis of kinetic data that the ease of these substitution reactions and, especially, reactions of hydrolysis and solvolysis of β-chloroethyl alkyl sulfides and yperite can be explained by the intermediate formation of ethylene sulfonium ions [4]. The existence of such ions also explains the certain isomerization reactions and spatial rearrangements which occur during the hydrochlorination of β-hydroxy substituted sulfides [5] and acetolysis of β-halo substituted propyl aryl sulfides [6].

However, we failed to find any papers in which the problem of the substitution reactions of alkoxy groups in β-alkoxyethyl sulfides would have been examined from this viewpoint. The sole indication by Kretov [7] appears to show that β,β'-dialkoxydiethyl sulfides do not differ from other ethers of primary alcohols since they are readily cleaved by hydrogen iodide and bromide, but react only poorly with hydrochloric acid even on being heated.

Earlier in our papers [8, 9] with Shapiro we had found the methods of synthesis for various β-alkoxyethyl and β,β'-dialkoxydiethyl sulfides, starting with vinyl ethers [Equations (1, 2)]:

$$ROCH=CH_2 + R_1SH \rightarrow ROCH_2CH_2SR'. \quad (1)$$

$$2ROCH=CH_2 + H_2S \rightarrow (ROCH_2CH_2)S. \quad (2)$$

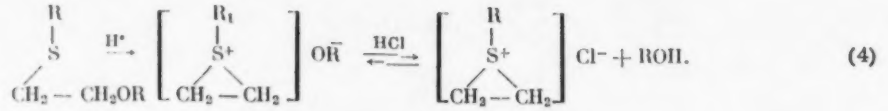
As should have been expected, an extreme mobility of the alkoxy group was discovered during the systematic study of the behavior of this group in these substances in respect to hydrogen chloride. The action of excess hydrogen chloride in dioxane medium at atmospheric pressure and moderate temperatures (20-50°) leads quite rapidly (20-25 hours) to the establishment of equilibrium [Equation (3)] which is severely shifted toward formation of the hydrochlorination product:

$$ROCH_2CH_2SAlK + HCl \rightleftarrows ClCH_2CH_2SAlK + ROH. \quad (3)$$

Thus, the corresponding chlorides are readily formed in up to 70-80% yields. Such a mobility of the alkoxy groups is not characteristic for the usual aliphatic ethers of primary alcohols which, as a rule, are cleaved only under very drastic conditions by hydrogen chloride [10]. Evidently, even the mechanisms of these two reactions differ materially. While the cleavage of the ethers usually proceeds through the formation of ions of the oxonium

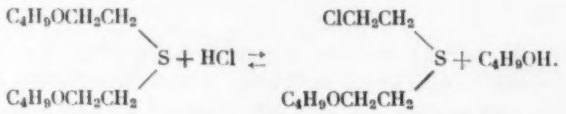
*Here the literature is so extensive that the present authors naturally do not claim the complete citation of all published papers.

type [10], all the regularities found by us for the β-alkoxyethyl sulfides are readily explained if one allows for the formation of ethylene sulfonium ions:



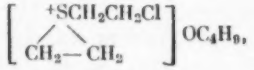
(4)

The ease of replacement of the alkoxy group by chlorine depends significantly on the structure of the other part of the molecule (R). Thus, 1-butoxy-2-phenylmercaptoethane does not react with hydrogen chloride at all without the use of elevated pressures and heating to 60-70° with excess hydrogen chloride in a sealed ampul is required, for the replacement of its alkoxy group. Evidently, the interaction of the electrons of the phenyl ring with the unshared electrons of the sulfur atom hinders the formation and the decomposition of the thionium ion.* In the case of β,β'-dibutoxydiethyl sulfide, the reaction with hydrogen chloride separates into two steps, just as the hydrolysis of β,β'-dichlorodiethyl sulfide may be kinetically separated into two steps [4]. The first butoxy group is readily cleaved by the action of hydrogen chloride under mild conditions:

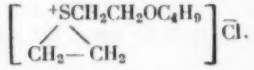


(5)

Introduction of one chlorine atom evidently hinders the formation of the ions

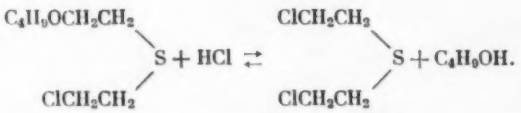


which are necessary for the further reaction, since ions



are formed more readily.

The second butoxy group may be replaced by heating in a sealed ampul with excess hydrogen chloride:



(6)

The conditions of the synthesis and the yields of the various alkyl (aryl) sulfides are given in Table 1. The resulting substances were used specifically in a study conducted jointly with Kabachnik, Mastriukova and their co-workers [11] in the synthesis of insecticidal compounds by alkylation of salts of dialkyl dithiophosphates.

The original β-alkoxy derivatives (1-alkoxy-2-alkyl(aryl)-mercaptans) were obtained by the reaction of vinyl ethers with mercaptans [Equation (2)] the conditions of running of which required some refinement in the present work.

It was shown earlier [8] that the addition of mercaptan to vinyl alkyl ethers proceeds contrary to the Markovnikov rule, after prolonged heating of ethylmercaptan with the ethers in the presence of traces of

* The same reason explains the stability of β-chloroethyl aryl sulfides, relative to β-chloroethyl alkyl sulfides, known in the literature [1].

TABLE 1

Synthesis of β-Chloroethyl Alkyl (Aryl) Sulfides From Corresponding β-Butoxy Derivatives

Formula		Method of synthesis*	Reaction conditions			Comp. of mixt. reaction	
of initial β-butoxy derivative	of resulting β-chloride		HCl in moles per mole of butoxy sulfide	Temperature in °C	Time in hrs.	Unreacted β-butoxy sulfide, in %	Chloride yield (%), based on reacted butoxy deriv.
$C_4H_9OCH_2CH_2SC_2H_5$	$ClCH_2CH_2SC_2H_5$	a	**	40—50 18—20	3 21	12—15	65—70
$C_4H_9OCH_2CH_2SC_2H_5$	$ClCH_2CH_2SC_2H_5$	b	2,3	60—70 18—20	14 58	60	60
$C_4H_9OCH_2CH_2SC_2H_5$	$ClCH_2CH_2SC_2H_5$	b	4,0	60—70 18—20	9 63	5	70—75
$C_4H_9OCH_2CH_2SC_4H_9$	$ClCH_2CH_2SC_4H_9$	a	**	30—50 18—20	3 21	5	75—80
$C_4H_9OCH_2CH_2SC_4H_9$	$ClCH_2CH_2SC_4H_9$	a	**	40—50 18—20	9 39	91	—
$C_4H_9OCH_2CH_2SC_4H_9$	$ClCH_2CH_2SC_4H_9$	b	2,5	60—70 18—20	14 58	85	10
$C_4H_9OCH_2CH_2SC_4H_9$	$ClCH_2CH_2SC_4H_9$	b	5,0	60—70 18—20	9 63	10	82
$C_4H_9OCH_2CH_2$ $C_4H_9OCH_2CH_2$ >S	$ClCH_2CH_2$ $C_4H_9OCH_2CH_2$ >S	1a	**	25—30	6	95	—
$C_4H_9OCH_2CH_2$ $C_4H_9OCH_2CH_2$ >S	$ClCH_2CH_2$ $C_4H_9OCH_2CH_2$ >S	a	**	40—60 15—18	4 20	10—20	70—75
$C_4H_9OCH_2CH_2$ $ClCH_2CH_2$ >S	$ClCH_2CH_2$ $ClCH_2CH_2$ >S	c	6,0	60—70 18—20	14 58	—	80

*The appropriate β-butoxy derivative was: a) treated with gaseous HCl in dioxane medium (flask with a stirrer); b) heated in a sealed ampul with HCl in dioxane (see in more detail in Experimental).

**In experiments with method a) the amount of HCl was not taken strictly into account but considering the volumes of dioxane used and the solubility of HCl in it (25-27 weight %), it may be considered that this amount was not less than 5-7 moles per 1 mole of the β-butoxy derivative.

oxygen.* Mixtures which contain varying amounts of the isomeric monothioacetals were formed when this reaction was run in contact with air.

$$ROCH=CH_2 + C_2H_5SH \rightarrow \begin{matrix} ROCH_2CH_2SC_2H_5 \\ CH_3CH(SC_2H_5)(OR) \end{matrix} \qquad (7)$$

In the present work we showed that in order to accelerate the reaction of vinyl alkyl ethers with ethylmercaptan and to obtain predominantly the desired 1-alkoxy-2-ethylmercaptoethanes, it is possible to run the process in the presence of 0.2-0.5 weight % of azoisobutyronitrile with a rather brief heating period. Isopropylbenzene hydroperoxide does not show any catalytic action at room temperature. It is interesting that this reaction

*The reactants were first frozen in the ampul which was then pumped down to 1-5 mm pressure and then sealed.

TABLE 2

1-Alkoxy-2-alkyl(aryl)mercaptoethanes

No. of compound	Formula of compound	B.p. in °C (p in mm of mercury)	n_D^{20}	d_4^{20}	MR found	MR calculated	Yield in %
1	$C_2H_5OCH_2CH_2SC_2H_5$	78—78,5 (35)	1,4507	0,9126	39,57	39,52	95—98
2	$C_4H_9OCH_2CH_2SC_2H_5$	55—57 (3)	1,4520	0,8979	48,77	48,78	95—98
3	$C_2H_5OCH_2CH_2SC_4H_9$	74,5—75 (7)	1,4530	0,8945	49,05	48,78	88
4	$C_4H_9OCH_2CH_2SC_4H_9$	101—102 (7)	1,4542	0,8873	58,15	57,99	94
5	$C_2H_5OCH_2CH_2SC_6H_5$	117—118 (7)	1,5432	1,0401	55,26	54,39	90
6	$C_4H_9OCH_2CH_2SC_6H_5$	128—128,5 (5)	1,5281	1,0064	64,36	64,63	96

is greatly accelerated by the presence of moisture. Moist ethylmercaptan adds rapidly and quantitatively to vinyl alkyl ethers, in the absence of initiators, the reaction being contrary to the Markovnikov rule and occurring, at times, with heat evolution. However, this reaction is so sensitive to negligible amounts of impurities that it is very difficult to reproduce its results and, for this reason, it is best to run the synthesis in the presence of azoisobutyronitrile. The more reactive mercaptans – butylmercaptan and thiophenol – added readily, contrary to the Markovnikov rule, even without added initiators. Some of the constants and the yields of the resulting 1-alkoxy-2-alkyl-(aryl)mercaptoethanes are given in Table 2, in which we also included the previously prepared 1-ethoxy- and 1-butoxy-2-ethylmercaptoethanes [8]. All these substances either do not contain any isomeric 1,1-substituted ethanes or contain not more than 2-5% of them, as indicated by the data from titration with sodium hydroxide after a treatment with alcoholic solution of mercuric chloride [12].

EXPERIMENTAL

I. Synthesis of 1-Alkoxy-2-alkyl(aryl)mercaptoethanes

Purified and distilled (immediately before the experiment) specimens of the vinyl ethers and the mercaptans were used in all experiments. All the reactions were run in excess vinyl ether.

1) 1-Butoxy-2-ethylmercaptoethane. Twenty g (0.2 mole) of vinyl butyl ether, 6.2 g (0.1 mole) of ethylmercaptan and 0.1 g of azoiso butyronitrile were sealed into an ampul, which had been flushed with dry nitrogen, and heated for six hours at 60°. The excess vinyl butyl ether (9.7 g) was distilled off under vacuum on the following day and was collected in a chilled trap. 15.6 (96.3%) of 1-butoxy-2-ethylmercaptoethane with b.p. 87-88.5° (11 mm) and $n^{20}D$ 1.4521 was isolated from the residue; the product agreed completely in its properties with the previously prepared material [8]; from the titration data [12] it contained less then 2% of the isomeric 1-butoxy-1-ethylmercaptoethane. Some of the experiments run under different conditions are shown in Table 3.

2) 1-Butoxy-2-butylmercaptoethane. Twenty g (0.2 mole) of vinyl butyl ether and 9.0 g (0.1 mole) of butylmercaptan were sealed into an ampul, previously flushed with dry nitrogen, and were heated for six hours at 60°. 17.3 g (93.5%) of 1-butoxy-2-butylmercaptoethane with b.p. 110-112° (8 mm) was isolated; the product contained 4-5% of the 1,1-isomer as shown by titration.

Found %: C 63.51; 63.06; H 11.68; 11.67; S 17.15; 16.95. $C_{10}H_{22}OS$. Calculated %: C 63.09; H 11.67; S 16.95.

If the reaction is run with the same proportions of the starting materials but without heating, there is formed after 48 hours a 96% yield of a mixture of butoxybutylmercaptoethanes containing 14-15% of the 1,1-isomer.

3) 1-Ethoxy-2-butylmercaptoethane was prepared by the same method (as in expt. 2) from butylmercaptan and vinyl ethyl ether; yield: 88%; free of 1,1-isomer; b.p. 74.5-75° (7 mm).

Found %: C 59.11; 59.02; H 11.17; 11.19; S 19.63; 19.70. $C_8H_{18}OS$. Calculated %: C 59.29; H 11.18; S 19.76.

*The reactants were first frozen in the ampul which was then pumped down to 1-5 mm pressure and then sealed.

4) 1-Ethoxy-2-phenylmercaptoethane was prepared by the same method in 90% yield from thiophenol and vinyl ethyl ether; b.p. 117-118° (7 mm); free of 1,1-isomer.

Found %: C 65.76; 65.87; H 7.75; 7.78; S 17.45; 17.44. $C_{10}H_{14}OS$. Calculated %: C 65.89; H 7.74; S 17.59.

5) 1-Butoxy-2-phenylmercaptoethane was prepared by the same method in 90-96% yield from thiophenyl and vinyl butyl ether; b.p. 128-128.5° (5 mm); contained 3-5% of 1,1-isomer.

Found %: C 68.85; 68.20; H 8.44; 8.44; S 14.96; 15.07. $C_{12}H_{18}OS$. Calculated %: C 68.52; H 8.63; S 15.25.

II. Synthesis of β-Chloroethyl Alkyl(aryl) Sulfides

1-Butoxy-2-alkyl(aryl)mercaptoethanes were used as starting materials in all experiments. The reaction proceeds readily with the corresponding ethoxy derivatives but mixtures of products are formed whose components differ but little in their boiling points. All yields are calculated on the reacted 1-butoxy-2-alkyl(aryl)mercaptoethane.

1) 1-Chloro-2-ethylmercaptoethane. Thirty ml of dioxane was saturated with dry hydrogen chloride with stirring in a three-necked flask with a reflux condenser. Temperature rose to 50°. Ten g (0.062 mole) of 1-butoxy-2-ethylmercaptoethane was added. Passage of hydrogen chloride and stirring were continued at this temperature for three hours after which the mixture was set aside overnight. Excess hydrogen chloride was removed on the following day by blowing with dry air, after which dioxane and the resulting butanol were distilled off under vacuum of 60-80 mm; then were obtained the following fractions:

Fraction I, 40-68° (47 mm), 1 g
Fraction II, 68-71° (47 mm); 5.1 g
Fraction III, 71-113° (47 mm); 0.2 g
Fraction IV, 113-115° (47 mm); 1.2 g

1-Chloro-2-ethylmercaptoethane (fraction II, yielded 66%) had, after repeated distillations, a b.p. of 78-79° (52 mm), $n^{20}D$ 1.4878, d^{20}_4 1.0689; found MR 31.58; calculated MR 33.51. Literature data [3]: b.p. 63-65° (47 mm), d^{25}_4 1.0663.

Fraction IV was the unreacted sulfide.

2) 1-Chloro-2-butylmercaptoethane. 15.1 g of 1-chloro-2-butylmercaptoethane with b.p. 111-114° (16 mm) was obtained in the same manner from 23 g of 1-butoxy-2-butylmercaptoethane in 50 ml of dioxane; yield: 81.9%. The substance had b.p. 66° (5 mm), 73° (7 mm), $n^{20}D$ 1.4828, d^{20}_4 1.0164, after repeated distillations; found MR 42.85; calculated MR 42.745. Literature data [13]: b.p. 58-59° (1 mm), d^{25}_4 1.0122.

3) 1-Chloro-2-β-butoxyethylmercaptoethane. 17.0 g (72%) of 1-chloro-2-(β-butoxyethyl)mercaptoethane with b.p. 98-101° (3 mm) was obtained by this method from 30 g (0.11 mole) of β,β'-dibutoxydiethyl sulfide (prepared by the action of hydrogen sulfide on vinyl butyl ether [9]) and 90 ml of dioxane; the product had b.p. 101-102° (3 mm), $n^{20}D$ 1.4778, d^{20}_4 1.0337, after repeated distillations; found MR 53.86; calculated MR 53.62.

Found %: S 16.21; 16.20; Cl* 16.94; 17.1. $C_8H_{17}OSCl$. Calculated %: S 16.29; Cl 18.02.

4) 1-Chloro-2-phenylmercaptoethane. 1-Butoxy-2-phenylmercaptoethane was recovered totally unchanged after a treatment analogous to that described in experiments 1-3. For synthesis of this chloride 20.3 g (0.1 mole) of 1-butoxy-2-phenylmercaptoethane, 25 ml of dioxane, were placed into an ampul provided with an adapter containing a capillary tube passing into the neck of the ampul and, after chilling the lower part of the ampul with liquid nitrogen, 18.3 g (0.5 mole) of dry hydrogen chloride was condensed in it. The cooled ampul was sealed and left for one day at room temperature (in a thick-walled metal pipe) after which it was heated for nine hours at 60-70°. After distillation, three days after the beginning of the experiment,** we isolated 14.2 g (82%) of 1-chloro-2-phenylmercaptoethane with b.p. 114.5-116° (7 mm). The product had b.p. 90-91° (1 mm), $n^{20}D$ 1.5814, d^{20} 1.1735, after repeated distillations; found MR 49.18; calculated MR 48.38. Literature data [13]: b.p. 88-89° (0.637); d^{25} 1.1769.

*Chlorine was determined alkalimetrically by back-titration of the alkali after shaking a sample of the chloride for four hours with excess 0.1 N aqueous sodium hydroxide. The determination was probably not quite quantitative.
**Excess HCl was first evaporated prior to distillation of the product; for this, the ampul was cooled with liquid nitrogen, opened and raised gradually to room temperature.

TABLE 3

Reaction of Vinyl Butyl Ether and Ethylmercaptan

Used for the reaction (moles)		Initiator (in weight %)	Reaction conditions		Overall yield in %	Reaction products (comp. in %)	
vinyl butyl ether	ethyl-mercaptan		temp. in °C	time (hours)		1,2-substituted	1,1-substituted
0,2	0,1	—	20—22	70	27	85,2	14,8
0,2	0,1	Water ~0,1%	20—22	24	99	97,5	2,5
0,2	0,1	Isopropylbenzene hydroperoxide 2.5%	20—22	24	12,4	31,5	68,5

5) β,β'-Dichlorodiethyl sulfide. 9.8 g (0.05 mole) of 1-chloro-2-(β-butoxyethyl)mercaptoethane and 20 ml of dioxane were placed in an ampul into which was condensed 11 g (0.31 mole) of dry hydrogen chloride. This was heated for 14 hours at 60-70°. 6.1 g (80% of theoretical) of β,β'-dichlorodiethyl sulfide, with b.p. 79-80° (2.5 mm) was isolated after distillation.

SUMMARY

1. The reaction conditions for vinyl alkyl ethers and mercaptans were refined, allowing one to prepare predominately the addition products which were contrary to the Markovnikov rule. A series of 1-alkoxy-2-alkyl(aryl)-mercaptoethanes was obtained in good yield.

2. It was shown that the alkoxy group in 1-alkoxy-2-alkyl(aryl)mercaptoethanes may be readily replaced by chlorine. A series of 1-chloro-2-alkyl(aryl)mercaptoethanes was synthesized by the following reaction sequence:

$$C_4H_9OCH=CH_2 \xrightarrow{RSH} C_4H_9OCH_2CH_2SR \xrightarrow{HCl} ClCH_2CH_2SR.$$

3. It was suggested that the reaction proceeds through formation of an ethylene sulfonium ion which permits one to understand the dependence of the ease of substitution of the alkoxy group on the structure of the other parts of the original sulfide, found in this work.

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A STUDY IN THE FIELD OF LACTONES AND LACTAMS

12. VINYL ETHER OF N-(β-HYDROXYETHYL)-PYRROLIDONE

F. P. Sidel'kovskaia, M. G. Zelenskaia and M. F. Shostakovskii

A series of nitrogen-containing vinyl compounds was prepared during the recent years, these compounds having some interesting properties, as for example vinyl lactams (I) [1] and vinyl ethers of β-ethanolamines (II) [2]:

$$CH_2=CHN\underline{(CH_2)_nCO} \quad \text{(I) (where } n = 3, 4, 5),$$

$$CH_2=CHOCH_2CH_2N\begin{matrix}R_1\\ \diagup\\ \diagdown\\ R_2\end{matrix} \quad \text{(where } R_1 \text{ and } R_2 = C_6H_5,\ C_2H_5,\ H \text{ in various combinations)}$$

It was of interest to synthesize some vinyl ethers of N-(β-hydroxyethyl)-lactams and to study their properties in comparison with the vinyl ethers of N-substituted β-enthanolamines, on one hand, and with vinyl lactams, on the other hand. In this paper we describe the vinyl ether of N-(β-hydroxyethyl)-pyrrolidone (III)

$$CH_2=CHOCH_2CH_2N\underline{(CH_2)_3CO}. \quad \text{(III)}$$

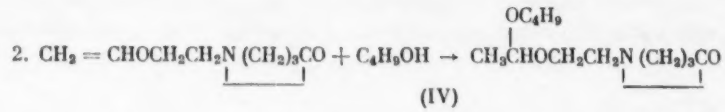
We failed to synthesize the vinyl ether of N-(β-hydroxyethyl)-piperidone. In an attempt to prepare the initial N-(β-hydroxyethyl)-piperidone by a method similar to that used in the synthesis of N-(β-hydroxyethyl)-pyrrolidone [3], we observed the formation of a product which was evidently N-(β-hydroxyethyl)amide of δ-hydroxyvaleric acid formed by the opening of the six-membered ring:

$$1.\ \overline{(CH_2)_4COO} + NH_2CH_2CH_2OH \rightarrow \underset{OH}{CH_2}-(CH_2)_3C\begin{matrix}O\\ \diagup\\ \diagdown\\ NHCH_2CH_2OH\end{matrix}$$

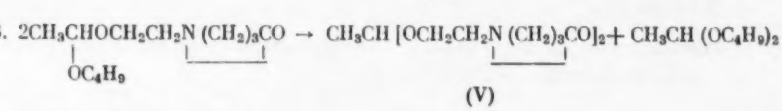
Vinyl ether (III) was obtained in good yield (70%) by vinylation of N-(β-hydroxyethyl)-pyrrolidone in the presence of either sodium alcoholate or potassium hydroxide as the catalyst. As is known, the vinylation of pyrrolidone (I) occurs smoothly only in the presence of the previously prepared alkali salt of this lactam. Since the vinyl ether of β-(diphenylamino)-ethanol, in the class of vinyl ethers of β-ethanolamines, is the closest in structure to ether (III), it was rational to compare specifically these two substances.

β-(Diphenylamino)ethanol is vinylated with good yield in the presence of potassium hydroxide or potassium alcoholate (yield of 65-75%) [2]. It was found that vinyl ether (III) is quantitatively hydrolyzed by 2% sulfuric acid at the temperature of 23-25° in the course of 30 minutes (57% in the absence of the acid). Vinylpyrrolidone is hydrolyzed under these conditions to the degree of 85% [4]. Vinyl ether (III) adds alcohols in the presence of catalytic amounts of concentrated hydrochloric acid. Thus, butyl N-(ethylpyrrolidonyl) acetal (IV) was isolated

from the reaction with butanol. Along with the mixed acetal we isolated the corresponding symmetric acetals: di-(N-ethylpyrrolidonyl) acetal (V) (28%) and dibutyl acetal, formed as the result of disproportionation of the mixed acetal.



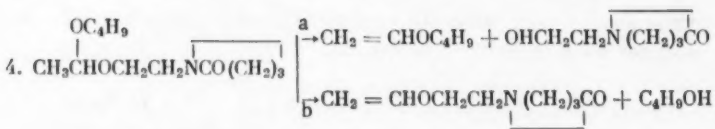
(IV)

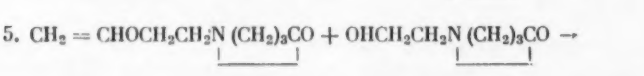


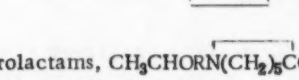
(V)

Addition of alcohols to vinyl lactams under the conditions mentioned above (on an example of vinylcaprolactam) occurs with low yields (about 10%) [5], while in the reaction of the vinyl ether of β-(diphenylamino)-ethanol with alcohols the mixed acetals are indeed formed, but are unstable and immediately suffer a series of transformations – disproportionation and decomposition of the mixed acetals [2].

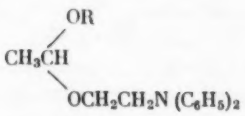
The thermal decomposition of mixed acetal (IV) is quite interesting; as a result of it we isolated vinyl butyl ether, butanol and acetal (V). In all probability, the decomposition of acetal (IV) proceeds in two directions simultaneously (a and b in Equation 4). The resulting vinyl butyl ether and butanol distil off during the reaction while the vinyl ether (III) and N-(β-hydroxyethyl)-pyrrolidone yield acetal (V) by reacting with each other.







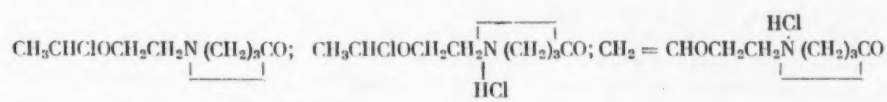
It has been shown that alkoxyethylidenecaprolactams, $CH_3CHORN(CH_2)_5CO$, form alcohol and vinyl lactam during thermal decomposition (direction b) [5], while acetals of structure:



yield decomposition products – vinyl alkyl ether and diphenylaminoethanol (direction a), even during vacuum distillation (2-3 mm), along with the disproportionation products [4].

In the reaction of the vinyl ether of N-(β-hydroxyethyl)pyrrolidone with hydrogen chloride there is formed an unstable product (VI) which is completely transformed into the hydrochloride of hydroxyethylpyrrolidone merely on standing for four days.

We failed to isolate substance (VI) in the pure state owing to its considerable instability. It is possible that a mixture of the following substances is formed in the reaction of hydrogen chloride with ether (III):



In order to clarify the tendency of the vinyl ether of N-(β-hydroxyethyl)-pyrrolidone to polymerize, we studied its behavior on heating, to the action of hydrogen peroxide and to azoisobutyronitrile. It was found that this ether polymerizes in a low yield (up to 34%) under the influence of 30% hydrogen peroxide. Under the conditions under which vinylpyrrolidone is polymerized in a yield of 62% [6], vinyl ether (III) forms but 8% of the polymer. Better results were obtained with polymerization under the influence of azoisobutyronitrile (Table 1). It is evident from Table 1 that with decrease of the amount of catalyst used the relative viscosity of the polymer increases, but the yield declines, while the latter is raised by increased duration of the process.

TABLE 1

Polymerization of Vinyl Ether of N-(β-Hydroxyethyl)-pyrrolidone; Initiator – Azoisobutyronitrile; Temperature 60° *

No. of expt.	Amount of initiator used in % of monomer	Duration of reaction in hours	Polymer yield in %	Relative viscosity η^{25} of 3% aqueous solution
1	0.5	36	31.7	1.4069
2	1	36	43.0	1.3530
3	0.5	100	38.8	1.4990
4	1	100	50.4	1.3806

*The thermal polymerization of vinyl ether of N-(β-hydroxyethyl)-pyrrolidone does not occur under these conditions.

It was shown that vinyl ether (III) does not form thermal polymers in 100 hours at 60°, while 8% of polymer is formed in 7 hours at 140-145°, and 34% polymer is formed in three hours at 270-300°.

Thus it is evident from the above that vinyl ether of N-(β-hydroxyethyl)-pyrrolidone is more reactive in ionic reactions and less reactive in radical reactions in comparison with vinyl lactams. It should be noted in a comparison of this ether with vinyl ether of β-(diphenylamino)-ethanol, that these compounds have rather close properties, especially in their ionic reactions.

EXPERIMENTAL

1. Synthesis of Vinyl Ether of N-(β-Hydroxyethyl)-pyrrolidone

The initial N-(β-hydroxyethyl)-pyrrolidone was prepared by a condensation of monoethanolamine with butyrolactone [3] and had: b.p. 138-139° (1.5 mm), $n^{20}D$ 1.4961, d^{20}_4 1.1423. Literature data: b.p. 142-143° (2.3 mm) [3]. Acetylene (about 2 moles) was introduced under pressure of 17-18 atmospheres into a steel autoclave (2 liter volume) containing 103.0 g of N-(β-hydroxyethyl)-pyrrolidone, 100 ml of dry dioxane and 4 g of powdered potassium hydroxide and the whole was heated for 12 hours at 150-160°. A tarry portion precipitated when the reaction product was treated with dry ethyl ether (400 ml); this was separated from the filtrate. The residue after the distillation of the solvents was vacuum distilled.

Fraction I, 112-135° (4.5 mm), 98.5 g
Fraction II, 150-159° (6 mm), 3.25 g
Tarry residue 15.5 g.

Repeated distillation of Fraction I gave 86.7 g (70%) of the vinyl ether of N-(β-hydroxyethyl)-pyrrolidone with b.p. 100.5-102° (2 mm), $n^{20}D$ 1.4876, d^{20}_4 1.0630; found MR 42.03; calculated MR 42.07.

Found %: C 61.57; 61.63; H 8.59; 8.35; N 9.05; 9.07. $C_8H_{13}O_2N$. Calculated %: C 61.91; H 8.44; N 9.02.

The resulting vinyl ether (III) gives the characteristic iodoform test [7]. Hydrolysis of vinyl ether (III) in 0.2 N solution of sodium bisulfite (sample of about 0.2 g, temperature 23-25°, duration 30 minutes) proceeded to ~ 57%; the percent hydrolysis reaches 99-99.5% under similar conditions but with addition of 2% sulfuric acid.*

*The technique of running the hydrolysis of vinyl lactams was described earlier [4].

2. Reaction of Vinyl Ether on N-(β-Hydroxyethyl)-pyrrolidone with Butanol

One drop (0.03 g) of concentrated hydrochloric acid was added to a mixture of 15.5 g of vinyl ether (III) and 7.4 g of butanol; a spontaneous heating to 60° was observed. Then the reaction mixture was heated for four hours at 90-93°, neutralized with potassium carbonate and distilled. After a number of distillations we isolated:

1) 9.0 g (43.7%) of Butyl N-(ethylpyrrolidonyl) acetal: b.p. 130-133° (1.8 mm), $n^{20}D$ 1.4615, d^{20}_4 1.0136; found MR 62.13; calculated MR 61.65.

Found %: C 62.60; 62.54; H 10.00; 9.81; N 6.40; 6.37. $C_{12}H_{23}O_3N$. Calculated %: C 62.85; H 10.10; N 6.11.

2) 3.95 g (27.8%) of di-(N-ethylpyrrolidonyl) acetal: b.p. 219-220° (1.5 mm), $n^{20}D$ 1.4979, d^{20}_4 1.1450; found MR 72.78; calculated MR for $C_{14}H_{20}O_4N_2$ 72.40.

Found %: C 58.85; 58.90; H 8.40; 8.51; N 9.46; 9.66; M 283.8; 278.1. $C_{14}H_{20}O_4N_2$. Calculated %: C 59.13; H 8.50; N 9.85; M 284.34.

3. Thermal Decomposition of Butyl N-Ethylpyrrolidonyl Acetal

13.7 g of the acetal was heated for two hours at 270-300° in the presence of 1% hydroquinone* in a Favorskii flask connected to a distilling condenser, receivers and a trap cooled to −40°. After 10 minutes of heating decomposition was observed which was accompanied by distillation of a substance with b.p. 60-100°, $n^{20}D$ 1.4001 (4.05 g); the trap contained 0.43 g of material with $n^{21}D$ 1.3992. After redistillation of these products we isolated: 1.36 g of butanol with b.p. 115-117°, $n^{20}D$ 1.3989; 2.17 g of a product with b.p. 92.5-93.5°, $n^{20}D$ 1.4008, in which 95.84-96.46% of vinyl butyl ether was determined by the bisulfite method. The remaining reaction mixture was vacuum distilled.

Fraction I, 100-133° (2.7 mm); 1.33 g; $n^{20}D$ 1.4880
Fraction II, 134-142° (2.7 mm); 2.33 g; $n^{20}D$ 1.4869
Fraction III, 217-221° (1-1.5 mm); 3.93 g; $n^{19.5}D$ 1.4972.

Fraction III was di-N-(ethylpyrrolidonyl) acetal. The weight of a tarry residue in the distillation flask was 1.52 g.

4. Addition of Hydrogen Chloride to Vinyl Ether (III).

A stream of hydrogen chloride was passed into a solution of 10 g of freshly distilled vinyl ether (III) in 10 ml of absolute ethyl ether, cooled to −10°, at such a rate as to maintain the reaction temperature below 5°. The duration of reaction was 2 hours. Excess hydrogen chloride was removing by blowing with a stream of dry nitrogen, the ethyl ether was distilled off under vacuum, the remaining residue was dissolved in 5 ml of benzene and reprecipitated with ether; dried under vacuum (7-10 mm) for one hour, the product of addition of hydrogen chloride to ether (III) (the substance was denoted by symbol VI) weighed 11.56 g. Substance (VI) was hygroscopic.

a) Bisulfite determination of product (VI). A sample of product (VI) (about 1 g) was dissolved in a 100 ml volumetric flask. Ten ml portions of the solution were then taken for determination of HCl by alkalimetry and for a separate determination of acetaldehyde (by the bisulfite method: a mixture of the solution with sodium bisulfite was kept for 30 minutes at 23-25°).

TABLE 2

Results of Determination of HCl and Acetaldehyde in Hydrolysis Products of Substance (VI)

Duration of storage of reaction product in hours	Product (VI) determined via acetaldehyde in %*	% HCl*
Directly after the experiment	67.57	28.18
24	61.63	20.74
48	10.33	29.80

*Content of acetaldehyde and HCl was calculated for a compound with formula $C_8H_{14}O_2NCl$ (theoretical content of HCl 18.98%).

*Hydroquinone was used to suppress the polymerization of vinyl ether III.

Similar analyses were run for product (VI) after it had been stored for 24 and 48 hours: substance (VI) was reprecipitated from benzene solution with ethyl ether and vacuum dried prior to each such determination. The analytical results are given in Table 2.

The addition product (VI) lost its ability to dissolve in benzene after 64 hours following its isolation from the reaction mixture; at this juncture it became a crystalline hydrochloride of hydroxyethylpyrrolidone; m.p. 80-83°, after recrystallization from ethylene chloride. A mixed melting point with an authentically prepared sample of the hydrochloride prepared by passage of hydrogen chloride into the hydroxyethylpyrrolidone at −5°, gave no depression.

Found %: HCl 21.30; 21.25. $C_6H_{12}O_2NCl$. Calculated %: HCl 22.01.

5. Polymerization of Vinyl Ether (III)

a) Under the influence of azoisobutyronitrile. The experiments were run in ampuls into which we placed 3-10 g of vinyl ether (III) and an appropriate amount of azoisobutyronitrile; the contents were heated to 60° for a definite period, after which they were cooled and treated with ethyl ether. The precipitated polymer was washed additionally with ether and vacuum dried. After the removal of ether from the extracts we isolated the remaining monomer by vacuum distillation in the presence of 1% hydroquinone.

The results of the experiments are given in Table 1.

b) Under the influence of hydrogen peroxide. 10 g of vinyl ether (III) was heated to 143-144° and 0.2572 g of 29.6% hydrogen peroxide was added with stirring in 0.09 g portions every two hours. The temperature of the reaction mixture rose to 152° after the addition of the first portion of the catalyst. No heat evolution was observed after the addition of the last portion of the catalysts. Duration of the reaction was seven hours. The reaction product was treated with ethyl ether (15 ml) whereby 3.46 g of the polymer was isolated in the form of a viscous liquid (34.6%); after having been reprecipitated from a benzene solution with ethyl ether the relative viscosity (at 25°) of its 3% aqueous solution was 1.126. Some 4.16 g of unreacted monomer was isolated from the ether extracts.

c) Thermal polymerization of vinyl ether (III). Ten g of vinyl ether (III) was heated for seven hours at 140-145°. The reaction mixture was distilled in the presence of 1% hydroquinone; 8.26 g of the monomer was obtained with b.p. 93-96° (2 mm) and 1.16 g of residue was left. 0.81 g of polymer (8.1%) was isolated from this residue by solution in benzene and reprecipitation with ethyl ether; relative viscosity of 3% aqueous solution of this polymer at 25° was 1.073. Heating 2 g of vinyl ether (III) to 270-300° for three hours gave 0.99 g of polymer (34%); relative viscosity of its 3% aqueous solution at 25° was 1.133; 0.64 g of monomer was recovered.

d) Under the influence of 0.2% benzoyl peroxide. 3.7 g of vinyl ether (III) and 0.0075 g of benzoyl peroxide were heated in an ampul 36 hours at 60°. The reaction mixture was distilled in the presence of 1% hydroquinone. 3.60 g of vinyl ether (III) with b.p. 108-109° (3.2 mm) was isolated.

6. Reaction of Valerolactone with Monoethanolamine

The initial δ-valerolactone was synthesized from 5-chloropentanoic acid [8] and had the following constants: b.p. 90-94° (7 mm), $n^{22}D$ 1.4545.

Literature data: b.p. 92° (8 mm), $n^{20}D$ 1.4550 [9]. Valerolactone changes to a polymer with m.p. 38-39° (M 912, 836) in storage.

Found %: C 59.57; 59.52; H 8.20; 8.20. ($C_5H_8O_2$). Calculated %: C 59.61; H 8.05.

Literature data [9]: M.p. 35-40°, M 1060, 1060.

13.1 g of freshly distilled δ-valerolacetone and 9.7 g of monoethanolamine were heated with stirring for nine hours at 190-200°.

Vacuum distillation yielded:

Fraction I, 92-131° (2-2.5 mm); 0.3 g
Fraction II, 132-163° (2-2.5 mm); 1.5 g; $n^{20}D$ 1.4800

Fraction III, 164-180° (2-2.5 mm); 4.5 g; $n^{20}D$ 1.4960
Fraction IV, 181-220° (8.7 g); $n^{20}D$ 1.5003
Residue 5.0 g
Trap contents 0.6 g, $n^{21}D$ 1.3509.

Decomposition was observed during the fractionation. Fractions III and IV crystallized; they were combined and recrystallized from acetone: m.p. 49.5-51.5°.

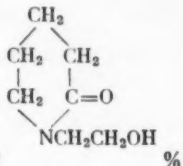
Found %: C 52.92; 52.93; H 9.53; 9.49; N 9.22; 9.14.

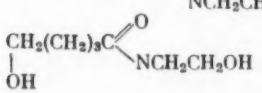
Since decomposition of the product was observed during ordinary vacuum distillation (2-2.5 mm), the above reaction was repeated and the products were distilled in high vacuum:

Fraction I, 136-137° ($1.3 \cdot 10^{-5}$ mm)
Fraction II, 138-140° ($1.3 \cdot 10^{-5}$ mm), m.p. 56-59°.

Fraction II was soluble in water, dioxane and ethanol, insoluble in ethyl and petroleum ethers.

Found for Fraction I %: C 54.30; 54.12; H 9.30; 9.43; N 10.01; 10.24; hydroxyl number 729, 723.
Found for Fraction II %: C 52.49; 52.36; H 9.47; 9.38; N 9.27; 9.25; hydroxyl number 651.

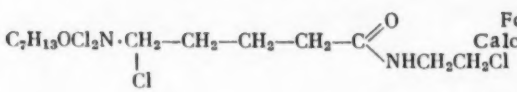
Calculated for  %: C 58,71; H 9,14; N 9,78
hydroxyl number 391

 %: C 52,15; H 9,38; N 8,69;
hydroxyl number 695

To 7 g of the condensation product of δ-valerolacetone and monoethanolamine, recrystallized from acetone and dissolved in 18 ml of benzene, we added dropwise with stirring at 9-10° 6 g of freshly distilled thionyl chloride over 30 minutes. The reaction mixture formed two layers. Vacuum distillation of the lower layer gave the following fractions:

Fraction I, 102-124° (3 mm), 0.5 g
Fraction II, 125-130° (3 mm), 2.73 g, m.p. 120-121° (from acetone).
Tarry residue 3.13 g.

An additional 0.52 g of the product with b.p. 127-131° (3.5 mm) was isolated from the upper layer after distillation of benzene.

 Found %: C 42,60; H 6,86
Calculated %: C 42,42; H 6,61

SUMMARY

1. Vinyl ether of N-(β-hydroxyethyl)-pyrrolidone was prepared.

2. The reaction of δ-valerolacetone with ethanolamine at about 200° was investigated. Evidently under these conditions an opening of the six-membered ring occurs.

3. It was shown by an example of a reaction of addition of butanol that vinyl ether of N-(β-hydroxyethyl)-pyrrolidone can add alcohols. Di-N-(ethylpyrrolidonyl) acetal and butyl N-ethylpyrrolidonyl acetal were isolated.

4. Thermal decomposition of butyl N-ethylpyrrolidonyl acetal was studied.

5. It was shown that vinyl ether of N-(β-hydroxyethyl)-pyrrolidone adds hydrogen chloride. The resulting product is unstable and is transformed during storage into N-(β-hydroxyethyl)pyrrolidone hydrochloride.

6. It was found that vinyl ether of N-(β-hydroxyethyl)-pyrrolidone polymerizes under the influence of azoisobutyronitrile, hydrogen peroxide and is subject to thermal polymerization, but is not polymerized in the presence of 0.2% of benzoyl peroxide at 60°.

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* Original Russian pagination. See C. B. Translation.
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CARBONYLATION OF PARA-DICHLOROBENZENE

S. E. Iakushkina and N. V. Kisliakova

Reactions of carbon monoxide with aromatic and aliphatic halides have been studied very little. In 1931 Hoff [1] obtained acetic acid from methyl chloride and carbon monoxide in the presence of aluminum chloride. Frank and Theobold [2] repeated this reaction with polychlorinated methanes and obtained chloroacetic acids in accordance with the equations:

$$CCl_4 + CO \rightarrow CCl_3COCl. \quad (1)$$

$$HCCl_3 + CO \rightarrow HCCl_2COCl. \quad (2)$$

$$H_3CCl + CO \rightarrow H_3CCOCl. \quad (3)$$

However the need to use high pressures (950 atm) and the low yields of the resulting acids did not allow the carbonylation reaction to develop along these lines.

Groombridge [3] patented the method of preparation of fatty acids from chlorohydrocarbons, using nickel carbonyl and iodine as the catalyst. It was indicated in an American patent [4], that it is possible to prepare the dimethyl ester of terephthalic acid in about 10% yield from para-dichlorobenzene, carbon monoxide and methyl alcohol. In 1954 Yamamoto and Sato [5] examined the reaction of carbon monoxide with various aromatic halogen compounds and found that iodobenzene reacts most rapidly while dichlorobenzene reacts most slowly. It appeared interesting to us, in this connection, to run a systematic study of the reaction of carbon monoxide with dichlorobenzenes and to establish the dependence of the direction of the reaction on the factors which influence it.

EXPERIMENTAL

In the present work this problem was investigated using for an example the carbonylation of para-dichlorobenzene. For compounds with a mobile hydrogen atom we took water and methyl alcohol, while as the catalyst we used the complex $[(C_6H_5)_3P]_2 \cdot NiBr_2 \cdot C_4H_9Br$ and a combination of iodine and metallic nickel.

The para-dichlorobenzene used for the reaction had m.p. 53°. The experiments were run in a rotating stainless steel autoclave with the capacity of 250 cc. The autoclave was charged in succession with para-dichloro benzene, water or alcohol, the catalyst and carbon monoxide at 80-90 atm pressure. The autoclave was heated to the desired temperature by means of an electric furnace. The temperature was regulated by an electronic thermoregulator. After completion of the reaction, the residual pressure was released and the gaseous reaction products were passed through slit-scrubbers to remove the hydrogen chloride and into receivers cooled to −78°. The uncondensed gas was isolated for analysis. The autoclave contents were washed with water to remove nickel salts and the residue was dissolved in ethyl ether. The insoluble portion was terephthalic acid, which was isolated in pure form by precipitation with acid from a hot alkaline solution. para-Chlorobenzoic acid was isolated from the ethereal solution in a similar way. The unreacted para-dichlorobenzene was extracted from the ethereal solution.

The gas analysis was run with a VTI gas analyzer. The isolated acids were characterized, after purification and recrystallization, by their acid numbers and by the melting points of methyl esters prepared from them. The

TABLE 1

Carbonylation of p-Dichlorobenzene in Presence of Water

Expt. no.	p-Dichlorobenzene (moles)	Water (moles)	Catalyst	Medium	Temp. of expt., °C	Maximum pressure in atm	Duration of expt. in hours	Reaction products: terephthalic acid, % of theoret.	Reaction products: p-chlorobenzoic acid, % of theoret.	Reaction products: benzene, % of theoret.	H_2 in %
1	1	1,47	$[(C_6H_5)_3P]_2NiBr_2C_4H_9Br$	Benzene	290	250	2,0	25,2	75,5	—	—
2	1	1,64	8,5 g Ni 1 g I_2	»	300	350	1,0	17,0	82,1	—	—
3	1	2,0	5g Ni 1 g I_2	—	200	280	1,0	19,8	59,9	21,2	9,5
4	1	2,0	5 g Ni 1g I_2 + Cu	—	200	270	1,5	15,9	33,8	50,4	—
5	1	8,2	10 g Ni 1 g I_2	—	300	320	1,0	15,5	63,5	22,2	—
6	1	8,2	5 g Ni 1 g I_2	—	370	450	1,5	—	—	85	—
7	1	8,2	5 g Ni 1 g I_2 + Cu	—	270	220	1,5	9,7	39,2	51,5	—
8	1	8,2	5 g Ni 1 g I_2	—	260	220	1,5	19,0	49,7	32,0	—
9	1	8,2	5 g Ni 1 g I_2 + Cu	—	300	260	1,0	11,0	25,4	63,8	20,0

TABLE 2

Carbonylation of p-Dichlorobenzene in Presence of CH_3OH

Expt. no.	p-Dichlorobenzene (moles)	Methyl alcohol (moles)	Water (moles)	Catalyst	Reaction temp., °C	Maximum pressure, atm.	Duration of expt., hours	Reaction products: terephthalic acid, %	Reaction products: p-chlorobenzoic acid, % of theoret.	Reaction products: dimethyl terephthalate, % of theoret.	Reaction products: methyl benzoate, % of theoret.	H_2 in %
1	1	7,6	—	Complex	250	250	9		Reaction failed to proceed			
2*	1	7,6	—	»	350	400	1	12,1		22,0		
3	1	4,5	2,7	3,2 g Ni 0,5 g I_2	300	300	1		15,7		84,6	3,9
4	p-Chlorobenzoic acid 1	4,5	1,1	0,5 g I_2	300	240	1	5,3		67,4	31,6	4,9

*The yields are calculated on p-dichlorobenzene charged.

esters produced as the result of the carbonylation reaction were characterized, after recrystallization or distillation, by their ester numbers and melting or boiling points. The benzene which was isolated was determined by its boiling point and index of refraction. The experimental results are given in Tables 1 and 2.

Carbonylation reaction occurs as the result of interaction of para-dichlorobenzene with carbon monoxide and water both in the presence and the absence of solvents, and yields terephthalic and para-chlorobenzoic acids. Simultaneously a conversion of carbon monoxide in accordance with the equation: $CO + H_2O \rightleftharpoons CO_2 + H_2$ occurs with an intensity which depends on the amount of water used for the reaction and the reaction temperature. Benzene was also found among the reaction products. The appearance of this substance may be explained by elimination of the halogen in para-dichlorobenzene by the liberated hydrogen. It is known that hydrogen cleaves halogen from an aryl halide molecule in the presence of metallic nickel and yields of hydrocarbon [6].

The experimental data obtained by us indicate that predominately benzene is formed at high temperature and with excess water. Simultaneously much hydrogen is evolved. Under the optimum conditions (Expt. No. 1, 3 and 8) para-chlorobenzoic and terephthalic acids are formed predominantly. The yields of para-chlorobenzoic acid calculated on the reacted para-dichlorobenzene are quite high and reach 80% of theoretical. The yields of terephthalic acid failed to rise over 25% of theoretical. The explanation for this may be found in the following. One may suppose that the first stage of the carbonylation reaction is the rupture of the carbon-halogen bond with addition of one molecule of carbon monoxide to para-dichlorobenzene and formation of an intermediate acyl chloride.

para-Chlorobenzoic acid or its ester is first formed by the action of water or alcohol, after which reaction addition of a second molecule of carbon monoxide results in terephthalic acid or its neutral ester. Side reactions occur simultaneously, hydrogen being formed as the result. With accumulation of hydrogen in the reaction mixture, the reaction of elimination of chlorine by hydrogen begins to compete with the carbonylation reaction and among the reaction products some benzene appears while in the presence of methyl alcohol there appears the methyl ester of benzoic acid (Table 2). The presence of nickel with well developed surface (formed from nickel carbonyl) aids the progress of such reactions. Only the elimination reaction proceeds at high temperature and with excess water (Expt. No. 6 in Table 1). Dimethyl terephthalate is formed in yields up to 67% of theoretical in carbonylation of para-chlorobenzoic acid in the presence of methyl alcohol. Simultaneously the formation of methyl benzoate is observed.

Thus we may regard the first stage of the carbonylation reaction of para-dichlorobenzene as the formation of para-chlorobenzoic acid. The replacement of the second chlorine atom by the carboxyl group is hindered by the secondary reactions of elimination whose rate is greater under the experimental conditions used than the rate of the carbonylation of the resulting para-chlorobenzoic acid. A special experiment on carbonylation of para-chlorobenzoic acid showed that it is possible to obtain terephthalic acid from it in sufficiently high yields.

SUMMARY

1. It was established that terephthalic and para-chlorobenzoic acids are formed in the carbonylation of para-dichlorobenzene in the presence of nickel catalysts.

It was shown that under the optimum conditions the yields of terephthalic acid reached 25%, and those of para-para-chlorobenzoic acid – 80% of theoretical.

2. It was shown that dimethyl terephthalate is formed in yields up to 67% of theoretical in the subsequent carbonylation of para-chlorobenzoic acid in the presence of methyl alcohol.

3. A supposition was made that the carbonylation of para-dichlorobenzene has a stepwise nature, in which para-chlorobenzoic acid is the intermediate product in the formation of terephthalic acid.

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SYNTHESIS OF POLYARYLENEALKYLS

9. SYNTHESIS AND TRANSARYLATION OF MONOFLUORO- AND MONOCHLORODIPHENYLMETHANES

G. S. Kolesnikov, V. V. Korshak and T. V. Smirnova

Continuing the study of the transarylation reaction of diarylalkanes, we attempted to determine whether or not the derivatives of diarylalkanes can participate in the transarylation reaction which is operative among the unsubstituted diarylalkanes [1-3]. For the study objects we selected monofluoro and monochloro derivatives of diphenylmethane, having the halogen atom in the aromatic ring. In case of transarylation of such monohalogen derivatives of diphenylmethane one could also follow the effect of the halogen present in the nucleus on the strength of the carbon–carbon bond between the aromatic nucleus and the methylene group, since the content of the halogen in the transarylation products would permit the calculation of the content of $-C_6H_4CH_2-$ groups and $-C_6H_3XCH_2-$ groups among the transarylation products.

The monohalogen derivatives of diphenylmethane, which were needed for this study, were prepared by us in the following manner. p-Chlorodiphenylmethane and m-chlorodiphenylmethane were prepared by the reaction of the appropriate chlorobenzyl chlorides with benzene in the presence of aluminum chloride. An attempt to prepare o-dichlorodiphenylmethane by this method was unsuccessful; instead of o-chlorodiphenylmethane we isolated a substance with m.p. 74-75°, while o-chlorodiphenylmethane melts at 13°, according to the literature data [4]. This substance corresponds to monochlorodibenzylbenzene in its chlorine content (found % Cl 11.95, 11.96; calculated chlorine content equals 12.13%); this substance was not studied further by us.

m-Fluorodiphenylmethane was prepared by the reaction of m-fluorobenzyl chloride with benzene in the presence of aluminum chloride. p-Fluorodiphenylmethane was prepared as follows: p-nitrobenzyl chloride was prepared by chlorination of p-nitrotoluene and its reaction with benzene in the presence of aluminum chloride gave p-nitrodiphenylmethane. The latter was reduced to p-aminodiphenylmethane and the amino group in the latter was replaced by fluorine by transformation of p-aminodiphenylmethane into the diazonium fluoborate and decomposition of the latter. An attempted synthesis of o-fluorodiphenylmethane, like the attempted synthesis of o-chlorodiphenylmethane, proved to be fruitless and as the result of condensation of o-fluorobenzyl chloride with benzene in the presence of aluminum chloride we isolated, instead of the expected o-fluorodiphenylmethane, a substance which contained the amount of fluorine which corresponded to its content in monofluorodibenzylbenzene (found %: F 7.17, 7.42; calculated content of fluorine is equal to 6.88%); this substance was not studied further. Thus, we synthesized four monohalogen derivatives of diphenylmethane which were then subjected to transarylation in the presence of aluminum chloride.

The transarylation of chloro derivatives of diphenylmethane was run at 150° since one could have expected the formation of chlorobenzene as a reaction product of low molecular weight; the temperature was maintained above the boiling point of chlorobenzene to insure its complete removal from the reaction zone. The catalyst concentration was 7.5 mole % and the duration of the reaction was four hours. The results are given in Table 1.

It is evident from Table 1 that p-chlorodiphenylmethane and m-chlorodiphenylmethane do enter the transarylation reaction under the influence of aluminum chloride and form a polymer. Determination of the chlorine content in the resulting polymer from p-chlorodiphenylmethane showed that it was but 12.05% and was considerably below the calculated amount of chlorine in a polymer composed of fragments $-C_6H_3ClCH_2-$; a

calculation showed that for each $-C_6H_3ClCH_2-$ fragment in this polymer there are present 1.88 fragments of $-C_6H_4CH_2-$. Consequently, a copolymer of phenylenemethyl and chlorophenylenemethyl is formed as the result of transarylation of p-chlorodiphenylmethane. A polymer containing 16.36% of chlorine is formed as the result of transarylation of m-chlorodiphenylmethane, this substance being a copolymer of phenylenemethyl and chlorophenylenemethyl units in which 1.08 fragments $-C_6H_4CH_2-$ are present for each fragment of $-C_6H_3ClCH_2-$. These results indicate that the rupture of the bond between the methylene group and the aromatic nucleus which carries the substituent occurs more readily in p-chlorodiphenylmethane than a similar rupture between the methylene group and the unsubstituted aromatic nucleus. This may be explained by the influence of the chlorine atom present in the para-position in respect to the methylene group. In case of transarylation of m-chlorodiphenylmethane, the chlorine atom, located in metaposition relative to the methylene group, evidently does not affect the bond strength between the methylene group and the aromatic nucleus which contains the chlorine atom and therefore a copolymer is formed which contains nearly equal amounts of phenylenemethyl and chlorophenylenemethyl residues as the result of transarylation of m-chlorodiphenylmethane.

We ran the transarylation of the monofluoro derivatives of diphenylmethane at 110° with the catalyst concentration of 7.5 mole % and the reaction duration of four hours. The results are given in Table 2.

TABLE 1

Transarylation of m- and p-Chlorodiphenylmethanes

Name of substance	Isolated		Molecular weight of polymer
	starting material in % on amount taken for reaction	polymer in % of theoretical	
p-Chlorodiphenylmethane	9.9	84.8	2300
p-Chlorodiphenylmethane	5.9	84.8	1990
m-Chlorodiphenylmethane	19.8	93.7	870
m-Chlorodiphenylmethane	17.8	89.3	960

TABLE 2

Transarylation of m- and p-Fluorodiphenylmethane

Name of substance	Isolated		Molecular weight of polymer
	starting material in % on amount taken for reaction	polymer, in % of theoretical	
p-Fluorodiphenylmethane	9.5	63.0	1440
m-Fluorodiphenylmethane	43.0	51.8	940
m-Fluorodiphenylmethane	23.6	70.3	1520

It is evident from Table 2 that the monofluoroderivatives of diphenylmethane enter the transarylation reaction on being heated with aluminum chloride and form products with high molecular weight. The determination of fluorine content in the polymer prepared by transarylation of p-fluorodiphenylmethane showed that it was equal to 6.47%. A calculation showed that 2.06 fragments $-C_6H_4CH_2-$ were present in the resulting copolymer per each $-C_6H_3FCH_2-$ fragment. A copolymer containing 9.62% fluorine was obtained in transarylation of m-fluorodiphenylmethane; 0.99 phenylenemethyl residues are present in this copolymer per each fluorophenylenemethyl residue.

Thus, in the transarylation of monofluoro derivatives of diphenylmethane, the halogen located in metaposition relative to the methylene group does not exert any influence on the strength of the carbon-carbon bond between the methylene group and the aromatic nucleus, while the halogen located in para-position relative to the methylene group weakens the bond of the latter group with the aromatic nucleus which contains the substituent.

EXPERIMENTAL

m-Chlorobenzyl chloride. 100 g of m-chlorotoluene was placed in a 250 ml flask, provided with a reflux condenser, a chlorine inlet tube and a thermometer, and this was chlorinated at 160-165° under illumination until

a 27.2 g weight gain was reached. The flask content, after completion of the chlorination, was blown for 30 minutes with nitrogen, after which it was vacuum distilled. Fraction with b.p. 112-114° (25 mm) was collected. The yield of m-chlorobenzyl chloride was 78.7 g or 61.8% of theoretical.

m-Chlorodiphenylmethane. 300 ml of dry benzene and 4 g of powdered anhydrous aluminum chloride were placed in a 500 ml flask, provided with a reflux condenser and a dropping funnel; the mixture was heated to boiling on a water bath after which 48.3 g of m-chlorobenzyl chloride was added dropwise to the boiling benzene; the refluxing was continued for 30-40 minutes after which the mixture was cooled and poured into a mixture of ice and hydrochloric acid. The benzene solution was washed 3-4 times with water, dried for 2-3 hours with calcium chloride and freed of benzene by distillation. The residue was vacuum distilled, with the fraction having b.p. 168-175° (255 mm) being collected. 31.9 g of m-chlorodiphenylmethane was obtained which corresponded to 52.4% of theoretical. m-Chlorodiphenylmethane boiled at 160-162° (25 mm) after a redistillation.

p-Chlorobenzyl chloride was prepared by chlorination of p-chlorotoluene at 180-190° under illumination until a weight gain of 27.2% of the weight of the starting material was reached. p-Chlorobenzyl chloride with b.p. 96-98° (10 mm) was isolated; yield: 83% of theoretical.

p-Chlorodiphenylmethane was prepared like m-chlorodiphenylmethane. 31.4 g of p-chlorodiphenylmethane with b.p. 147-149° (5 mm) was isolated from 48.3 g of p-chlorobenzyl chloride and 350 ml of benzene in the presence of 4 g of aluminum chloride; yield: 51.7% of theoretical.

m-Fluorobenzyl chloride was prepared by chlorination of m-fluorotoluene (synthesized from m-toluidine through the diazonium fluoborate) at 155-160° until weight gain of 30-35% of the weight of initial m-fluorotoluene was reached. The yield of m-fluorobenzyl chloride with b.p. 79-80° (10 mm) was 85.5% of theoretical.

m-Fluorodiphenylmethane was prepared like m-chlorodiphenylmethane. 15.2 g of m-fluorodiphenylmethane with b.p. 123-125° (4 mm) was isolated from 43 g of m-fluorobenzyl chloride and 300 ml of benzene in the presence of 4 g of aluminum chloride; yield: 27.5% of theoretical.

p-Nitrobenzyl chloride was obtained by chlorination of 150 g of p-nitrotoluene at 190° up to weight gain of 38.8 g; the blowing with nitrogen to remove hydrogen chloride was done at elevated temperature, since the reaction mixture crystallized at room temperature. After three recrystallizations from alcohol we isolated 56 g of p-nitrobenzyl chloride with m.p. 71°; yield: 29.8% of theoretical. According to literature data the melting point of p-nitrobenzyl chloride is 71° [5].

p-Nitrodiphenylmethane was prepared by condensation of 51.5 g of p-nitrobenzyl chloride with 350 ml of benzene in the presence of 4 g of aluminum chloride. The yield of the product with b.p. 178-181° (4 mm) was 41.5 g or 65.2% of theoretical.

p-Aminodiphenylmethane was prepared by reduction of p-nitrodiphenylmethane with tin in hydrochloric acid [6]. 30 g of p-aminodiphenylmethane was obtained from 41.5 g of p-nitrodiphenylmethane; yield: 84.6% of theoretical.

p-Fluorodiphenylmethane was prepared by the technique described for the synthesis of fluorobenzene [7]. 8.4 g of p-fluorodiphenylmethane, which distilled at 106-107° (4 mm), was isolated from 45 g of p-aminodiphenylmethane hydrochloride; yield: 25% of theoretical.

SUMMARY

1. m- and p-chloro derivatives and m- and p-fluoro derivatives of diphenylmethane were synthesized and it was shown that they undergo the transarylation reaction on being heated in the presence of aluminum chloride. m-Chloro-, m-fluoro- and p-fluorodiphenylmethanes were synthesized for the first time.

2. It was found that the halogen atoms located in para-position relative to the methylene group of diphenylmethane weaken the bond between the methylene group and the substituted aromatic nucleus; the halogen atoms located in meta-position relative to the methylene group do not exert any influence on the strength of this bond.

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BRIEF COMMUNICATIONS

PREPARATION OF 1,6-ANHYDROGLUCOFURANOSE IN THERMAL DECOMPOSITION OF CELLULOSE UNDER VACUUM

O. P. Golova, N. M. Merlis and Z. V. Volodina

In this work we extended the study of the chemical composition of the solid distillate formed by thermal decomposition of cellulose under vacuum. The solid distillate, formed from cellulose in up to 75% yield, contains up to 70% of levoglucosan, along with carbonyl compounds, acids and their derivatives (substances with the ester group). The isolation of a neutral product from the solid distillate, accomplished with the anion exchange resins [1], and its subsequent separation from levoglucosan by crystallization led to the isolation of a sirupy product which contained 72% of substances which show an increase of the reducing power after being hydrolyzed (the percentage is calculated on glucose anhydride), the sirupy product having zero optical activity.

The study of the sirupy product showed that it contained the dextrorotating isomer of levoglucosan – 1,6-anhydroglucofuranose. The presence of 1,6-anhydroglucofuranose was proved by the following scheme [2]: the sirupy product was acetylated with acetic anhydride in pyridine and the acetate was distilled under 0.5 mm pressure in the form of fractions with b.p. 112-140° and 140-150°; both fractions were freed of levoglucosan triacetate by crystallization from isopropyl alcohol, after which they were hydrolyzed with barium methoxide and oxidized with iodic acid to remove any residual levoglucosan. The 1,6-anhydroglucofuranose was isolated as the p-nitrobenzoate which was characterized by its specific rotation, melting point and elemental analysis. This ester, in its properties, was completely identical with the p-nitrobenzoyl derivative of 1,6-anhydroglucofuranose isolated previously from the products of thermal decomposition of starch under vacuum [2]. According to the preliminary calculation, from the specific rotation data of the sirupy product and the content of glucose anhydrides in it, it appeared that the yield of 1,6-anhydroglucofuranose based on cellulose is about 3%.

It was shown that the sirupy product does not contain any polymers; this proof was secured by propionation and distillation of the propionates in high vacuum [3].

SUMMARY

It was shown that 1,6-anhydroglucofuranose is formed in the thermal decomposition of cellulose under vacuum, the yield being 3% based on cellulose.

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X-RAY INVESTIGATION OF LINEAR POLYESTERS

Iu. V. Mniukh

A study of some polyesters by means of x-ray structural analysis was done some time ago by Fuller and his co-workers [1-4] who came to certain conclusions about the packing of the molecules of polyesters. However, these conclusions were inevitably incomplete owing to the selective character of the study and were also at times unfounded owing to the overevaluation of the possibilities of this method.

EXPERIMENTAL

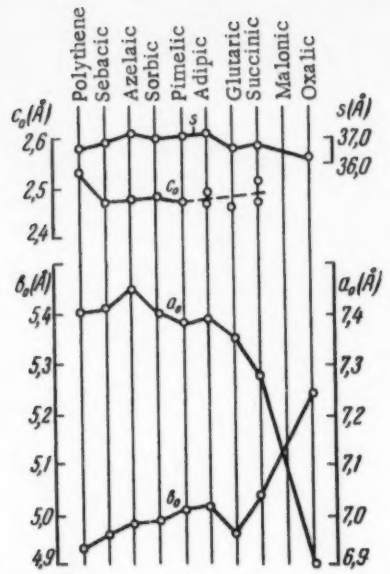
We had at our disposal some series of polyesters which are shown in the table. The Debye photographs from monochromatic radiation were secured for all these specimens. The table is divided approximately into three areas. The polyesters had a rhombic subcell* (or R-subcell) of the type of paraffins and polythene (area I) if their

Glucosides	Dicarboxylic acids: no. of CH_2 groups shown										
	CH_2	0	1	2	3	4	5	6	7	8	10
		Ox.	M	S	G	A	P	S	A	S	D
Ethylene glycol	2						II				
Trimethylene glycol	3						III				
Tetramethylene glycol	4										
Pentamethylene glycol	5						II				
Hexamethylene glycol	6										
Decamethylene glycol											
Eicosamethylene glycol							I				

Table of Linear Polyesters Formed by Various Dicarboxylic Acids (listed horizontally) and Glycols (listed vertically)

structure was basically determined by the packing of the methylene groups. Polyesters belonging to area III do not register in the R-subcell. Our attempts to determine the elementary subcell in them were fruitless. The existence of the transitional area II is quite natural. The x-rays of substances in this area do register the R-subcell, but these are less perfect than those in area I: the number of lines is decreased; lines (hko) may be still registered rather surely, but the deviation of d^{calc}_{hko} and d^{measd}_{hko} increases owing to the "loosening" of the subcell by oxygen atoms; the agreement of d^{calc}_{hkl} and d^{measd}_{hkl} becomes quite poor and these lines are actually absent from many of the x-rays, since the periodicity across the chain is preserved better than that along the chain.

*The subcell is constructed from the repeated vectors of the methylene groups [5].



Change of parameters a_0, b_0 and c_0 of the subcell, and $S = a_0 \cdot b_0 \cdot c_0$ for the series of decamethylene glycol. The data for polythene were taken from paper [6].

The cell dimensions for the series of decamethylene glycol esters are illustrated by the curves of the figure (above) which show a certain systematic trend of the parameters. We should note that the shortest acids – malonic and oxalic – display a jump in the properties: in the first case the samples are amorphous or semiamorphous, while in the second case there occurs a sharp change in the subcell parameters a_0 and b_0. This jump is also observed along other polyesters of these acids.

The lines on the x-rays from areas I and II may be readily separated into two groups. The majority of them belong to R-subcell, i.e., are registered with the formula:

$$\frac{1}{d^2} = \frac{h^2}{a_0^2} + \frac{k^2}{b_0^2} + \frac{l^2}{c_0^2},$$

when $a_0 \approx 7{,}4$ Å; $b_0 \approx 5{,}0$ Å; $c_0 \approx 2{,}5$ Å.

The remainder of the lines belong to the true cell, i.e., are caused by the atoms of oxygen of the C=O group. We are able to judge the disposition of the ester groups only in the case in which the dimensions of the true cell are known. Attempts to index the lines of the true cell were made through the following formula:

$$\frac{1}{d^2} = \frac{h^2}{a_0^2} + \frac{k^2}{b_0^2} + \frac{l^2}{c^2}\left[1 + \frac{m^2 c_0^2}{a_0^2} + \right.$$

$$\left. + \frac{n^2 c_0^2}{b_0^2}\right] \pm \frac{2hl}{a_0^2}\frac{c_0}{c}\, m \pm \frac{2kl}{b_0^2}\frac{c_0}{c}\, n$$

(c is the period of the true cell along the molecular axis), based on the assumption about the validity of the "shifted" model, which consists of the following: if the x-rays clearly show the R-subcell, the structure is determined by the packing of the methylene groups, while the ester groups "adjust themselves" to this packing. This presupposes that all possible structures may be exhausted by two vectors of shear mc_0 and nc_0 (for molecules bound by translation a_0 and b_0, respectively); here m and n are whole numbers. Results of this study showed that, as a rule, the indexing fails. Thus, the shear hypothesis to which Fuller adheres is contrary to the facts and thus we lose the sole basis on which one might make a selection of the true cells. This means that even in the case of preservation of the R-subcell, the oxygen atoms strongly modify the packing of the "polythene" type [6]. An exception is provided by polyesters with relatively small number of oxygen atoms in the chain, about which we shall write elsewhere.

SUMMARY

A large number of linear polyesters was examined by the x-ray powder method. In cases in which the structure was basically determined by the packing of the methylene groups, the former had the R-subcell of the type of paraffin and polythene, which was realized the more accurately the greater the number of carbon atoms in the chain. The dimensions of the subcell show the systematic alteration of parameters within the limits of the homologous series. The inconsistency of the "shear" hypothesis was established.

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CONCERNING THE INTERCONVERSION OF L-PROLYLGLYCINE DIKETOPIPERAZINE AND ITS DIPEPTIDES

K. T. Poroshin, T. D. Kozarenko and V. A. Shibnev

In the literature devoted to the problem of collagen structure an individual place is reserved for glycine and L-proline as the predominant amino acids and which determine the molecular configuration. The fact of the isolation of notable amounts of glycyl-L-proline and L-prolylglycine from collagen hydrolyzates provides the basis for supposing that both dipeptides are structural elements of the protein molecule. However, the variety of conditions under which the protein hydrolysis has been run by the various authors [1-3] does not allow one to express a definite decision about the predominance of glycyl-L-proline or L-prolyl-glycine dipeptides in the chain of collagen molecules. It is also necessary to consider the fact of interconversion of the dipeptides and the diketopiperazines corresponding to them, which fact had been noted previously [4].

A need arose in this connection to check the possibility of cyclization of glycyl-L-proline and L-prolyl-glycine into their anhydrides, as well as to check the possibility of hydrolysis of the anhydride to the corresponding dipeptides (Fig. 1). The experiments showed that even rather mild conditions suffice to form glycyl-L-proline readily in an alkaline medium from L-prolylglycine, while L-prolylglycine is formed in the acidic medium. A similar event was noted by several workers with other diketopiperazones [5]. Hydrolysis of L-prolylglycine anhydride does not go to completion and, as shown by our experiment, stops at some equilibrium position. Similar phenomena were observed by other workers with the examples of glycine and alanine anhydrides [6, 7]. We showed that the cyclization of both dipeptides into their anhydride was quite simple especially in the case

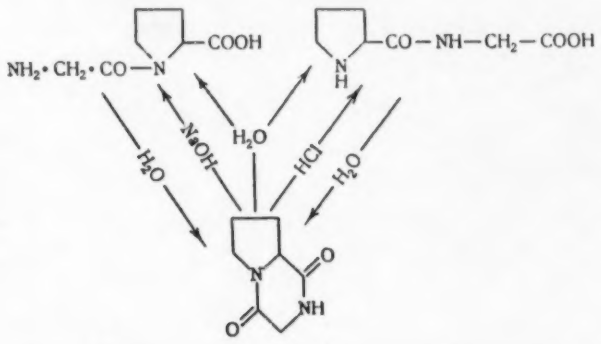

Fig. 1. Interconversion of L-prolylglycine diketopiperazine and its dipeptides.

of glycyl-L-proline and was possible even in a neutral medium. It is necessary to point out that this cyclization does not go to completion but stops at some equilibrium position. Thus, the ease of the interconversion of L-prolylglycine anhydride and its dipeptides must be kept in mind in the study of collagen structure.

EXPERIMENTAL

The hydrolysis products were identified by means of ascending chromatography; paper used was Whatman type B, crossed, made in Leningrad; the medium was butanol–water–acetic acid (4:1:5). The substances were deposited for tolidine development in amount of 200γ, while for isatin development we used 400γ samples. The results of the study are shown in Fig. 2.

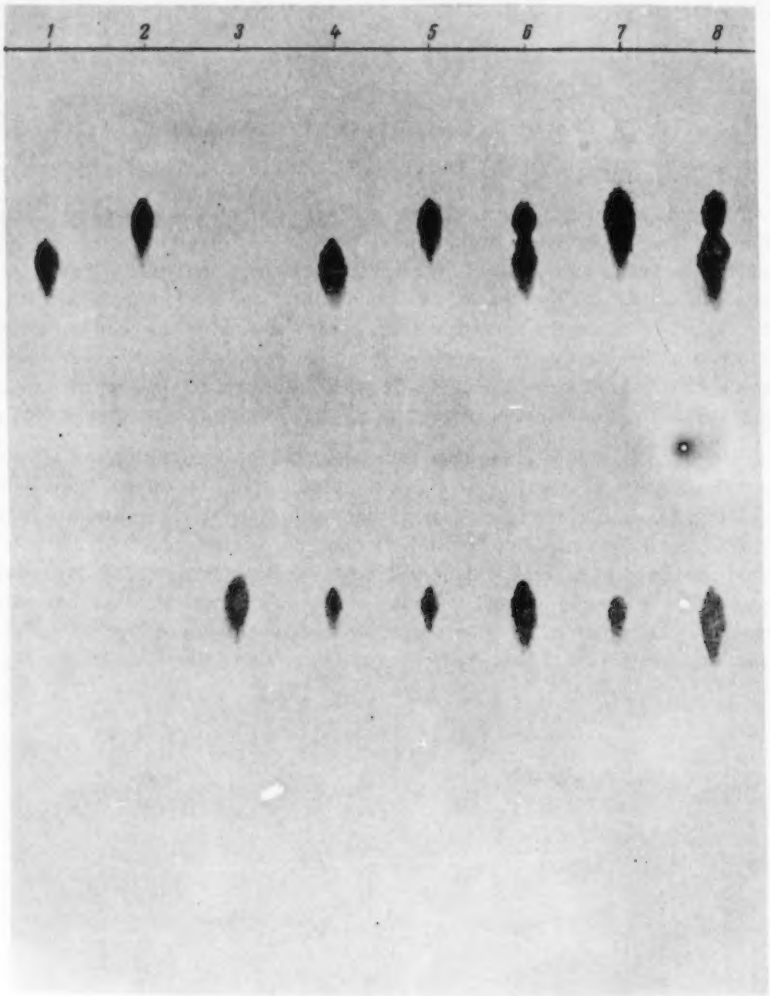

Fig. 2. Chromatogram developed with tolidine: 1) glycyl-L-proline; 2) L-prolylglycine; 3) L-prolylglycine anhydride; 4) L-prolylglycine anhydride in 0.1 N NaOH; 5) L-prolylglycine anhydride in 0.1 N HCl; 6) glycyl-L-proline in water; 7) L-prolylglycine in water; 8) L-prolylglycine anhydride in water.

L-Prolylglycine anhydride. L-Prolylglycine methyl ester (1 g) was heated under vacuum at 110° (vacuum of $1 \cdot 10^{-3}$ mm) for eight hours; the resulting anhydride was sublimed; yield 84% (0.7 g); m.p. 209-213°, $[\alpha]_D^{20}$ −217.4° (± 0.3) (c = 10 in water); R_f = 0.57.

Glycyl-L-proline. L-Prolylglycine anhydride (20 mg) was dissolved in 2 ml of 0.1 N sodium hydroxide and wat set aside for one hour at 40°. A yellow spot corresponding to glycyl-L-proline (R_f = 0.224) appeared after development of the chromatogram with isatin. Development with tolidine revealed a large amount of glycyl-L-proline and but little anhydride. While N sodium hydroxide leads to complete hydrolysis of the anhydride, the resulting dipeptide is simultaneously hydrolyzed by it to the amino acids.

L-Prolylglycine. L-Prolylglycine anhydride (20 mg) was dissolved in 2 ml of 0.1 N hydrochloric acid and was set aside for one hour at 40°. Then, 0.1 N sodium hydroxide was added until alkaline to phenolphthalein, after which the hydrolyzate was deposited on paper. A blue spot was revealed by development with isatin; this indicated prolylglycine (R_f = 0.187). Development with tolidine revealed the presence of a large amount of L-prolylglycine and a corresponding decrease of the anhydride. N-Hydrochloric acid does not hydrolyze the anhydride completely at 40°. In this case the hydrolyzate contains, in addition to the dipeptide, some free glycine and L-proline.

Hydrolysis of L-prolylglycine anhydride in water. L-Prolylglycine anhydride (20 mg) was dissolved in 2 ml of water and refluxed for 10-12 hours. After development with isatin there appeared a yellow spot which corresponded to glycyl-L-proline and a blue spot which corresponded to L-prolylglycine. Development with tolidine revealed both dipeptides in small amounts of considerable amounts of the anhydride.

Cyclization of glycyl-L-proline in water. Glycyl-L-proline (20 mg) was dissolved in 2 ml of water and refluxed for 10-12 hours. A yellow spot corresponding to glycyl-L-proline appeared on development with isatin, along with a blue spot corresponding to L-prolyiglycine. Development with tolidine showed the sharp prodominance of the anhydride and the presence of small amounts of both dipeptides.

Cyclization of L-prolylglycine in water. L-Prolylglycine (20 mg) was dissolved in 2 ml of water and refluxed for 10-12 hours. A blue spot of L-prolylglycine was observed after development with isatin. Development with tolidine revealed mainly L-prolylglycine and a small amount of the anhydride.

SUMMARY

The conditions of interconversion of L-prolylglycine anhydride and the corresponding dipeptides were studied.

N. D. Zelinskii Institute of Organic Chemistry
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Received March 22, 1957

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*Original Russian pagination. See C. B. Translation.

A. V. Topchiev, B. A. Krentsel' and L. G. Sidorova

Dear Editor:

Various considerations relative to the mechanism of stereo-specific polymerization of α-olefins have been expressed recently in the periodical literature. Some experimental data, obtained by us during a study of the polymerization reaction of propylene in the present of the catalytic system of $TiCl_4$ and $(iso\text{-}C_4H_9)_3Al$, are of interest in this connection.

A study of the change of the molecular weight of the resulting polypropylene during the course of the reaction showed that only 15 seconds after the start of the reaction a high molecular weight product is formed, having for example the characteristic viscosity of 0.8, in decalin at 120°. It turned out that the duration of the reaction does not affect the alteration of the molecular weight of the polymer. Thus, the structural chains coincide with the kinetic chains in polymerization, i.e., the macromolecules grow rapidly to a limiting size under the given set of conditions.

This situation, based on a large number of experiments, provides the foundation to consider that a chain character of propylene polymerization exists. As to the activity of the catalytic complex, this changes drastically with time. The rate of polymerization changes sharply in accordance with the differential curve, the rate being in correspondence with the change in the activity of the catalyst complex. It is possible that the change in the catalytic activity of the complex is explained by the disappearance from it with time of the free radicals which were discovered by Shilov and Bubnov in the system of the catalysts being used by us.

Presently we are conducting a further and deeper study of the mechanism of action of catalytic organometallic complexes in the polymerization of propylene and other α-olefins.

Petroleum Institute
of Academy of Sciences USSR

Received May 29, 1958

INTERMOLECULAR INTERACTIONS IN ACETYLENE AND ITS DERIVATIVES

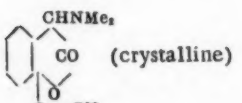
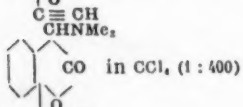
D. N. Shigorin, M. M. Shemiakin and M. N. Kolosov

Dear Editor:

Considering the peculiarities of chemical structure of acetylene and its derivatives, we supposed that these compounds could form complexes among themselves and with some solvents, these complexes being formed by the hydrogen bond $R-C\equiv C-H\ldots X$ ($X = O<$, $O=C<$, $N\lessdot$, $-C\equiv C$ etc.) Actually, a study of the infrared absorption spectra showed (see Table) a change in the frequencies of the $\equiv C-H$ groups and $-C\equiv C-$ groups in acetylene and its derivatives after solution in acetone, ether, pyridine and dioxane, as well as in transition from crystals to vapor or to solution in carbon tetrachloride (the relative displacement of the band of valence vibration of $\equiv C-H$ group reaches 4%).

This is evidently connected with the fact that the molecules of the acetylenes form complexes with the solvent molecules through a hydrogen bond of the type indicated above. Association of acetylene molecules, as

TABLE

Compound	ν(C–H) cm^{-1}	Δν(C–H) cm^{-1}	ν(C≡C) cm^{-1}
$C_6H_5C\equiv CH$ (liquid)	3290**	25	2080
$C_6H_5C\equiv CH$ in vapor	3315 (d)	0	2088
$C_6H_5C\equiv CH$ in CCl_4 (1 : 400)	3315 (d)	0	2088
$C_6H_5C\equiv CH$ in ether (1 : 100)	3248 (w) 3310	67	
$C_6H_5C\equiv CH$ in dioxane (1 : 10)	3250 (w)	65	
$C_6H_5C\equiv CH$ in acetone (1 : 10)	3255 (w)	60	
$HC\equiv CH$ (vapor)*	3373	0	1973
$HC\equiv CH$ (liquid)*	3341	32	1961
$HC\equiv CH$ in acetone*	3320	53	1960
$C_6H_5C\equiv CH$ in pyridine (1:10)	3220 (w,b) 3300 (d, f)	95	
			ν(C=O) cm^{-1}
 (crystalline)	3315 (d, f) 3210 (w, b)	0 105	1760
 in CCl_4 (1 : 400)	3315 (d)	0	1785
Same in pyridine (1:10)	3182 (w, b) 3300 (d, f)	133	1775

*K. Kohlrausch. Raman Spectra, Moscow, 1952, p. 77.

**d-diffuse, w-wide, b-bright, f-faint.

well as that of its homologs and derivatives, in liquid and solid states is evidently caused by the interaction of electrons in the $\equiv C-H$ bonds and $-C\equiv C-$ bonds belonging to different molecules as the result of which intermolecular electronic orbits arise, similarly to B_2H_6.

Thus we discovered a new phenomenon in the field of intermolecular interaction and showed experimentally a possibility of formation of hydrogen bond and of π-complexes with participation of molecules of acetylene and its derivatives.

It was established that hydrogen in the $\equiv C-H$ group is exchanged for deuterium after solution of the compound $R-C\equiv C-H$ in CH_3OD or C_2H_5OD. For $R-C\equiv C-D$ in carbon tetrachloride solution we found the bands: $\nu(\equiv C-D) = 2600\ cm^{-1}$, and $\nu(-C\equiv C-) = 1957\ cm^{-1}$.

L. Ia. Karpov Physicochemical Institute
and
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of Academy of Medical Sciences USSR

Received July 24, 1958

CURRENT EVENTS

ELECTION OF ACADEMICIANS AND CORRESPONDING MEMBERS OF THE ACADEMY OF SCIENCES USSR

Elections of academicians and corresponding members of the Academy of Sciences USSR took place in 1958 in the Academy of Sciences USSR: on 24-28 March in the Siberian Division of the Academy of Sciences USSR and on 16-20 June in all divisions of the Academy.

Fifteen candidates were proposed and registered for the six vacancies of corresponding members of the Academy of Sciences USSR which were announced January 28th of this year for the Siberian Division in the field of "chemistry." A binding condition in these elections was the agreement by the candidates to work in Siberia or in the Far East in institutions of the Siberian Division of The Academy of Sciences USSR. The general meeting of the Academy of Sciences USSR affirmed the corresponding members who had been recommended by the Division of Chemical Science and elected by the Siberian Division of the Academy of Sciences USSR in the field of "chemistry:" G. B. Bokii, G. K. Boreskov, V. V. Voevodskii, N. N. Vorozhtsov, A. A. Koval'skii and A. V. Nikolaev.

Georgii Borisovich Bokii – one of the leading scientists in the field of crystallography and crystallochemistry, author of over 120 published scientific papers and a number of textbooks. By widely applying the crystallographic methods of study to chemistry he developed an original scientific trend – crystallochemistry of inorganic substances. The cycle of his work has been devoted to the goniometric examination of the external form of crystals of inorganic compounds. He was the first to propose the use of goniometry as a method of physicochemical analysis. His studies in the technique of crystallo-optical measurements and its application to chemical problems have had a considerable significance as did the studies in the field of geometric crystallography. G. B. Bokii's work has created a new area – crystallochemistry of complex compounds. Jointly with S. S. Batsanov he developed the crystallo-optical method of determination of structures of complex compounds. Besides the optical method, he developed a method for quantitative determination of the magnitude of trans-effects by the measurement of interatomic distances in crystals of complex compounds.

Georgii Konstantinovich Boreskov – a well-known scientist, physicochemist, author of over 200 scientific publications and inventions in the field of chemical kinetics, catalysis and chemical technology. G. K. Boreskov's scientific activity began with the successful solution of a large techno-scientific problem – creation of a new vanadium catalyst for production of sulfuric acid. Simultaneously he conducted studies of other catalytic processes, conditions of their use and the scientific basis for the construction of catalytic contact equipment. In the monograph "Catalysis in production of sulfuric acid" published by G. K. Boreskov there are collected his papers on the study of reaction kinetics, clarification of the role of the processes of transfer of reactants to the catalyst surface, determination of optimum inner structure and grain dimensions of the catalyst, calculation of optimum temperatures and composition of gaseous mixture, etc. He was awarded the Stalin Prize in 1942 for his work in the field of sulfuric acid catalysis.

During the postwar period G. K. Boreskov has conducted studies on creation of scientific bases for selection and preparation of catalysts and development of new catalytic processes. The close connection of his studies with production problems and the study of the most important industrial processes made it possible for him to formulate clearly the paths for formation of a theory of heterogeneous catalysis. Developing ideas of D. I. Mendeleev and N. D. Zelinskii about the role of intermediate compounds in catalysis, he showed that the specific catalytic activity of a catalyst is determined, in the main, by its chemical composition and by the structure of the catalyst. His work on the effect of the processes of heat transfer and material transfer on the rates of catalytic reactions and on the selectivity of catalyst action had a considerable significance in the development of theory and practice

of catalysis. In recent years G. K. Boreskov has been successfully working in the area of new technology. In 1953 G. K. Boreskov was again awarded the Stalin Prize.

Vladislav Vladislavovich Voevodskii – an important specialist in the field of chemical kinetics and chemistry of free radicals. He developed a number of problems in theory of combustion, cracking and oxidation of hydrocarbons, heterogeneous and homogeneous catalysis, structure and properties of free radicals. V. V. Voevodskii established the significant details of the mechanism of the reaction of oxidation of hydrogen which is the classical example of branched chain reactions. A series of his papers in this area was terminated by publication, jointly with A. B. Nalbandian, of a monograph "Mechanism of Oxidation and Combustion of Hydrogen" (1949). V. V. Voevodskii introduced the concept of the role of heterogeneous factors into the theory of cracking of paraffin hydrocarbons. This permitted the explanation of a number of problems which failed to fit within the framework of Rice's theory. As a result of studies of the structure and the properties of free radicals, he discovered a new type of radical reaction and constructed a quantitative theory of cracking of olefinic hydrocarbons. Studying the processes of recombination of atomic hydrogen on surfaces of catalytically active substances, V. V. Voevodskii discovered two types of stationary processes – a low temperature one and a high temperature one – and determined the effectiveness of recombination on metallic and oxide catalysts. These results and a series of theoretical generalizations led V. V. Voevodskii jointly with N. N. Semenov and F. F. Vol'kenshtein to the creation of some radical chain concepts about the nature of the heterogeneous catalytic processes. Recently V. V. Voevodskii has been occupied by a study of the structure and properties of radicals in the condensed phase and by problems of heterogeneous catalysis.

Nikolai Nikolaevich Vorozhtsov – a great specialist in the field of organic chemistry, as well as technology of organic intermediates and dyes. N. N. Vorozhtsov's experimental and theoretical studies have expanded the chemistry of compounds of the aromatic series considerably. He studied in detail many reactions of substitution of aromatically bound halogen, the mechanism of catalytic isomerizations of halonaphthalenes with the use of labelled atoms, showed a number of interesting cases of replacement of chlorine atoms and nitro groups by fluorine, etc. N. N. Vorozhtsov also studied the reactions of halogenation of compounds of aromatic and aliphatic series, reactions of sulfonation and transformations of sulfonic acids. A group of his studies was devoted to the study of structure of some natural substances and to their synthesis. N. N. Vorozhtsov published a monograph "Chemistry of Natural Tanning Substances." N. N. Vorozhtsov has been devoting much attention to the development of theoretical problems of organic chemistry. In 1952 he was awarded the Stalin Prize.

Aleksandr Alekseevich Koval'skii – a great scientist in the field of kinetics of chemical reactions and nuclear physics. He took an active part in the creation of the chain theory. By examples of oxidation of phosphorus he established the fact that the upper ignition limit for chain oxidation reactions is set by the increased rate of reaction of homogeneous termination of chains at increased concentrations. A. A. Koval'skii measured accurately the position of the lower ignition limit in reactions of oxidation of hydrogen and carbon monoxide, was the first to study the kinetics of rapid self-accelerating processes in the course of the induction period by developing some original methods of recording of rapid processes. The fundamental work by A. A. Koval'skii in the study of the upper and the lower limits of ignition and kinetics of rapid oxidation reactions served as the experimental basis for the creation of the theory of branched chain reactions. Based on the work of A. A. Koval'skii and his co-workers in the study of high temperature oxidation of nitrogen, there was discovered the mechanism of this process which occurs through participation of free atoms of nitrogen and oxygen.

The second period of scientific activity of A. A. Koval'skii was devoted to the study of the mechanism of a number of heterogeneous catalytic reactions. It was proven, on the basis of the precise method of differential calorimetry developed by him, that certain heterogeneous reactions are in reality catalyzed only by the surface, while the main part of the process proceeds in gas phase by a radical chain mechanism. This provided the final confirmation of the position of the theory of heterogeneous-homogeneous catalysis.

A. A. Koval'skii is one of the pioneers in the study of nuclear physics of high energy particles. Experiments on absorption and multiplication of high energy neutrons, performed under his direction, have been a valuable contribution to the development of the so-called optical model of nuclei.

Anatolii Vasil'evich Nikolaev – a great scientist in the field of inorganic chemistry, author of over 100 scientific publications and a series of monographs on the study of natural salts, thermography and radiochemistry. A. V. Nikolaev's fundamental scientific work has been devoted to physicochemical analysis of salt systems for

the purpose of clarifying the conditions of formation of natural salts, means of their treatment and industrial utilization. Over a number of years he studied the saline deposits in Western Siberia and Kazakhstan, the salt lakes of Kulundinsk and Pavlodar, as well as Kuchuk Lake. A. V. Nikolaev lays claim to some remarkable studies of borates in Inder, the results of which are given in his monograph "Physicochemical Study of Natural Borates."

A . V. Nikolaev has aided the development, improvement and wide use of thermography, specifically in the area of complex compounds of platinum. Jointly with co-workers, he published the monograph "Thermography, Its Technique and Practice" and a collection "Protective Films on Salts;" containing new data on film formation on salt surfaces and the suggestions for use of such films. The most important work by A. V. Nikolaev in recent years has been the study of the chemistry and the separation of rare earth elements, the results of which study have been utilized by industry, and a large series of studies on extraction of inorganic substance by organic solvents.

* * *

On March 30 of this year the elections in all divisions of the Academy of Sciences USSR were announced for 26 vacancies of Academicians and 48 corresponding members of the Academy of Sciences USSR. In the Division of Chemical Science of the Academy of Sciences USSR with 16 vacancies (6 academicians and 10 corresponding members) there were recorded 112 candidates, including 20 for academicians and 92 for corresponding members. The largest number of candidates for corresponding members was proposed in the specialties of: technical chemistry – 32 candidates, organic chemistry – 25 candidates, physical chemistry – 17 candidates, etc.

On June 20 of this year the general meeting of the Academy of Sciences USSR elected in the Chemistry Division the following persons: to academicians A. A. Grinberg, M. I. Kabachnik, S. S. Medvedev, V. I. Spitsyn, I. V. Tananaev and M. M. Shemiakin, and confirmed the following corresponding members elected by the Division: A. N. Bashkirov, K. A. Bol'shakov, V. M. Vdovenko, B. A. Dolgoplosk, A. A. Korotkov, V. G. Levich, Iu. G. Mamedaliev, G. A. Razuvaev, O. A. Reutov, R. Kh. Freidlina, N. M. Emanuel, and S. Iu. Iunusov.

Academicians in the specialty of "Inorganic Chemistry"

Aleksandr Abramovich Grinberg – one of the greatest Soviet inorganic chemists, known for his work in the chemistry of complex compounds. The well founded studies by A. A. Grinberg have been devoted to problems of physicochemical foundation of the coordination theory, stereochemistry of platinum metals, oxidation-reduction transformations and acid-base equilibria in solutions of complex compounds, as well as chemical technology. A. A. Grinberg proposed a new method of determination of the structure of geometric isomers (Grinberg's method); he also created the coordination formulas of complex compounds of divalent platinum and created the stereochemistry of palladium; he developed a number of new volumetric methods of determination of platinum and iridium and, on the basis of extensive studies, expressed some interesting views on the mechanism of origin of the oxidation potentials of complex compounds of the platinum metals.

A. A. Grinberg extended the theory of acids and bases, originated by Kossel, to the complex ammoniates and provided the experimental support and confirmation for Bjerrum's theory of amino acids. Work on the magnetic susceptibility of platinum and palladium permitted him to clarify the bond character in the complex compounds of these metals. The sphere of his experimental and theoretical works has included the regularities of the trans-effect of I. I. Cherniaev. A. A. Grinberg was the first to propose the explanation for this phenomenon, based on polarization concepts. The experimental material gathered in recent years permitted him to describe the phenomenon of the cis-effect. A. A. Grinberg also studied extensively, not only the complex compounds of platinum, but also the derivatives of uranium, thorium, zirconium and other rare elements connected with the chemistry of nuclear fuels. We should especially note the systematic study of complex compounds of uranium performed by him.

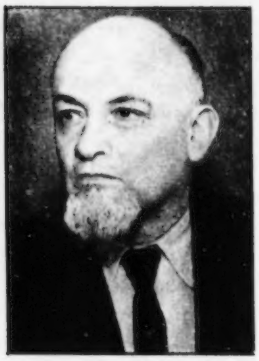
A. A. Grinberg is a pioneer in the field of application of labelled atoms for the study of equilibria and atomic mobility in complex compounds. Recently he has applied the isotope exchange, with other methods, to the solution of the problem of the mechanism of reactions of complex compounds in solutions. Simultaneously with important theoretical studies, he has solved a number of important problems of chemical technology. A. A. Grinberg has published about 130 scientific publications, including the monograph "Introduction into Chemistry of Complex Compounds" which won the Stalin Prize in 1946.

Viktor Ivanovich Spitsyn – a great scientist in the field of inorganic chemistry, chemistry and technology of rare and radioactive elements. His earlier work on chemistry of molybdenum and tungsten, specifically the study of composition of isopolytungstates and their reduction reactions, the preparation of chemically pure

Corresponding member
G. B. Bokii

Corresponding member
G. K. Boreskov

Corresponding member
V. V. Voevodskii



Corresponding member
N. N. Vorozhtsov

Corresponding member
A. A. Koval'skii

Corresponding member
A. V. Nikolaev

ammonium molybdate and others, were used already in the 1920's during the organization of production of tungsten and molybdenum in USSR. The work, carried out by him in 1928-1934, on the study of the reaction mechanism in the chlorination of oxides of beryllium, aluminum, niobium, tantalum and other elements, has played a large role, specifically in the organization of production of metallic beryllium. V. I. Spitsyn studied the problems of volatility and thermal stability of various inorganic substances: chlorides, sulfates and other compounds. Jointly with his co-workers he studied in detail, with the aid of modern physicochemical methods and, specifically, that of isotope exchange, the structure, the properties and the conditions of formation of the most important complex compounds of molybdenum and tungsten. As the result of these studies he proposed in 1957 a new theoretical treatment of the structure of aquopoly- and heteropoly compounds, an important class of inorganic complex compounds, this theory being based on some concepts of the hydrogen bond.

Over a number of years V. I. Spitsyn and his co-workers have been conducting extensive studies in the chemistry of uranium. He has studied the uranates of various metals, their composition and properties, the conditions of formation, crystal structure and thermal stability. These studies permitted him to present a theoretical basis for a number of industrial processes. In recent years a study of various radioactive isotopes and methods of their isolation and concentration has been conducted under V. I. Spitsyn's direction. He has also completed a number of studies on the isotope exchange of hydrogen and oxygen-18. In 1955 V. I. Spitsyn and his co-workers published the manual "Technique of Work with the Applications of Radioactive Indicators."

Ivan Vladimirovich Tananaev – one of the greatest scientists in the field of inorganic and analytical chemistry. His fundamental studies on the chemistry of fluorine and the application of physicochemical analysis to analytical chemistry of the rare elements are known well. Jointly with his co-workers, I. V. Tananaev has made studies of the chemistry of over twenty elements – lithium, rubidium, cesium, cerium, praseodynium, neodymium, samarium, titanium, zirconium, hafnium, niobium, tantalum, thorium, germanium, selenium, tellurium and uranium. I. V. Tananaev has devoted special attention to the study of composition, properties and reactivity of fluorides, oxalates, ferrocyanides and hydroxides, which has permitted him to discover a number of regularities and also to propose some valuable suggestions for the industry of rare metals and actinides. Thus, I. V. Tananaev and co-workers proposed the technological schemes for the extraction of rubidium and cesium from the saline raw material (ferrocyanide method), production of beryllium, actinides and other metals (fluoride methods).

At the present time I. V. Tananaev is working on problems of the chemistry of solutions of inorganic compounds. The simultaneous use in these studies of diverse physicochemical methods has permitted him to characterize more fully the state of the dissolved substances from the point of view of composition and stability. The especial stability discovered by I. V. Tananaev among the incompletely substituted ions containing fluorine, which determines the character of the dissolution process and the precipitation of fluorides, is now being widely used in analytical chemistry and in a number of industrial methods. I. V. Tananaev and co-workers proposed new analytical methods for the determination of a large number of elements, as well as impurities in pure substances, which have a considerable importance in modern technology. He has published over 170 scientific papers. The results of I. V. Tananaev's scientific activity have been twice noted by the Stalin Prize.

Academicians in the specialty of "Organic Chemistry"

Martin Izrailevich Kabachnik – one of the greatest Soviet organic chemists, known for his studies in the field of theoretical organic chemistry and the chemistry of organophosphorus compounds; author of over 170 scientific publications. M. I. Kabachnik's studies in the field of organic chemistry have been devoted to the examination of problems of tautomerism and dual reactivity. He developed a quantitative theory of tautomeric equilibrium as an acid-base protolytic equilibrium. Applications of this theory to the solution of concrete problems of tautomerism and chemistry of tautomeric substances has led to important results. Problems of the acidic properties of individual keto and enol forms, the effect of this acidity on the position of equilibrium and the role of solvents have been solved. A theoretical derivation of the previously known empirical formulas was accomplished and new potentiometric and calorimetric methods of determination of the tautomeric equilibrium constants were developed. Recently M. I. Kabachnik has been systematically studying the quantitative connection of structure of tautomeric forms with the position of equilibrium. M. I. Kabachnik's solution of the problem of participation of both geometric isomers of an enol in the tautomeric keto-enol equilibrium is interesting.

Academician A. A. Grinberg

Academician M. I. Kabachnik

Academician S. S. Medvedev

Academician V. I. Spitsyn

M. I. Kabachnik's synthetic studies in the field of organophosphorus compounds were done for the discovery of new substances of practical value, mainly the physiologically active ones, as well as for the development of new methods of synthesis. He has found a number of new methods of synthesis of organophosphorus compounds and accomplished the synthesis of many new types of these substances. During the years of the National War, M. I. Kabachnik completed a series of synthetic studies which were noted by the Stalin Prize in 1946. The systematic studies in the field of synthesis of new organophosphorus insecticides, begun by M. I. Kabachnik and his co-workers in 1953, have led to the preparation of new insecticides which are as active as the previously known ones but less toxic to man and animals. During this work over 200 new organophosphorus compounds were prepared and tested. One of these – Preparation M-81 – has been recommended for use in agriculture and its production adaptation is beginning.

Academician I. V. Tananaev

Academician M. M. Shemiakin

A considerable number of studies was completed by M. I. Kabachnik in the synthesis and study of the properties of α-aminophosphonic acids. These studies led to the preparation of organophosphorus complexes which have a high order of complex-forming ability. In all M. I. Kabachnik and co-workers have synthesized over 700 new organophosphorus compounds, some of which have a considerable practical interest.

Mikhail Mikhailovich Shemiakin – one of the greatest Soviet organic chemists, known for his work in the chemistry of natural and biologically active compounds, as well as in theoretical organic chemistry, synthetic chemistry and biochemistry. Over the past decade M. M. Shemiakin has developed particularly widely his studies of chemistry and biochemistry of antibiotics. He made a number of first-rate discoveries in this field, specifically in the chemistry of chloromycetin, a valuable antibiotic, the synthesis of which was first accomplished in his laboratory, after which the industrial production of its racemate (Sintomitsin) and the antibiotic itself (Levomitsetin) was organized. M. M. Shemiakin has developed various synthetic methods and accomplished the preparation of many analogs of chloromycetin. His further studies permitted him to make a number of important conclusions about the dependence of structure and the biological activity in this group of compounds, and to study the first steps of the mechanism of action of chloromycetin. These studies were the first to give the direction to an oriented search for highly active analogs of chloromycetin. Studies by M. M. Shemiakin in the field of chemistry of medicinally useful tetracycline antibiotics – aureomycin (Biomitsin), terramycin etc. – also have an important significance in that he solved the unclarified problem of their structure and recently developed the basic paths of synthesis of these complex compounds. M. M. Shemiakin recently accomplished the synthesis of the anticancer antibiotic sarcomycin; he also studied the structure, properties and the problems of biogenesis of a number of other antibiotics – streptomycins, Patulin, allycine etc. The modern state of chemistry of antibiotics was exhaustively treated in his fundamental monograph "Chemistry of Antibiotic Substance" which has come out in its second edition.

Important studies have been also made by M. M. Shemiakin in the field of chemistry and biochemistry of the vitamins. He developed and introduced into production some simple methods of synthesis of blood-clotting vitamin K_3 and its bisulfite compound. His theoretical studies in the field of vitamins of B_6 group led M. M. Shemiakin and A. E. Braunshtein in 1952-1953 to the quite important generalization of biochemistry – creation of the theory of the processes of amino acid metabolism catalyzed by the phosphopyridoxal enzymes. This theory permitted the explanation, from a unified viewpoint, of the reality of numerous types of biochemical processes. In recent years M. N. Shemiakin conducted a series of important studies in the chemistry of amino acids and

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peptides. He discovered a general path of synthesis of α-substituted α-amino acids, studied their properties and found the means of their introduction into peptides; he developed the general methods of synthesis for many amino acids labelled with C^{14} and N^{15}, now being produced for biological studies.

The many theoretical studies by M. M. Shemiakin have been devoted to the examination of the character and the mechanism of chemical reactions and for over twenty years he conducted studies on the oxidation-reduction transformations of organic compounds, which have led to important theoretical generalizations. M. M. Shemiakin has published over 140 scientific papers.

Academician in the specialty of "Chemistry of High Polymers"

Sergei Sergeevich Medvedev – one of the leading scientists in the field of chemistry of high polymers, expecially known for the studies in the area of polymerization processes. S.S. Medvedev created the theory of polymerization processes which is being successfully used in the solution of a number of practical problems in production of plastics and rubberlike materials. As the result of study of a wide range of polymerization processes, S. S. Medvedev was the first to establish the nature of many polymerization reactions as chain processes which proceed through free radicals. A detailed study of multilateral interactions of free radicals with substances present or formed in the polymerization media has led to the clarification of the mechanism of these processes, which in turn led to the possibility of control of the radical polymerization processes and of the regulation of the properties of the resulting polymers. The work of S. S. Medvedev in the study of emulsion polymerization has had considerable scientific and practical significance and, as a result of it, there were developed some new concepts about the mechanism of these processes, which unite the discovered experimental regularities. His studies in the field of ionic polymerization are quite interesting. S. S. Medvedev was the first to synthesize some new elastic materials with an improved thermal stability.

S. S. Medvedev obtained new and valuable data on radiation chemistry. He found ways of effective management of ethylene polymerization with the aid of radiation, with preparation of crystalline polyethylene. He clarified the peculiarities of grafting of polymers chains by cross-links under the influence of nuclear radiation. He established the peculiarities of action of radiation on multicomponent systems,these being connected with redistribution of the originally absorbed energy of radiation. He developed successfully the work in the field of thermo-oxidative decomposition of polymers with the purpose of their stabilization.

Work by S. S. Medvedev and his students has exerted a considerable influence on the development of the science of chemical kinetics of chain processes. S. S. Medvedev has published about 100 scientific papers; his studies in the field of polymerization processes have been rewarded by a Stalin Prize.

Corresponding Members of the Academy of Sciences USSR in the specialty of "Organic Chemistry"

Grigorii Alekseevich Razuvaev – a well-known organic chemist, who has devoted his studies to the chemistry of free radicals in solution and to chemistry of organometallic compounds. His most important studies were those on the transformations of free radicals generated in the medium of various solvents. Solvents participate actively, as a rule, in the reactions which are caused by free radicals. G. A. Razuvaev studied in detail the character of these reactions. The use of the method of labelled atoms played an important role in this work which allowed him to find the important factors of the rather complex interaction of free radicals with the solvents. G. A. Razuvaev established and studied a number of interesting cases of chain mechanism of reactions of free radicals in the liquid phase. For his studies in the chemistry of free radicals in solution G. A. Razuvaev was awarded the Lenin Prize in 1958.

G. A. Razuvaev's studies in the field of heteroorganic compounds were begun in 1928 with the study of the displacement of metals (mercury, tin, lead, arsenic, antimony, bismuth) from organic compounds by hydrogen under pressure, in various solvents. He devoted much attention to the study of organic derivatives of arsenic. He studied the action of ammonia on haloarsines, isolated the readily hydrolyzable primary reaction products, prepared arsenic derivatives of chlorostyrene, studied the oxidation of trivalent arsenic compounds with iodine, etc. He studied the nitration reactions as well as reactions of bromination and ring rupture of the heterocyclic arsenic compounds. G. A. Razuvaev has published over 180 scientific papers.

Rakhil Khatskelevna Freidlina – a great scientist in the field of organic chemistry and, specifically, chemistry of heteroorganic compounds. R. Kh. Freidlina's studies of the chemistry of organometallic compounds cover the compounds of metals: Mg, Hg, B, Tl, Si, Zr, Sn, Pb, As, Sb, and she had carried out a number of studies in the field of heteroorganic compounds on the chemistry of titanium, silicon and compounds of multivalent iodide. The most extensive studies were made by her in the field of telomerization reaction, transformation of telomers and the utilization of these reactions in industry.

R. Kh. Freidlina claims a number of important synthetic methods in the field of organometallic chemistry: she studied the dual behavior of saturated and unsaturated α- and β-substituted aliphatic compounds of mercury, lead, thallium, and showed that these compounds are true organometallic substances and not complex compounds. R. Kh. Freidlina studied in detail the chemistry of organic compounds of titanium, and prepared the first low polymers of the polytitanoxane type; she also developed the basic synthetic methods in this field. Later these methods were used and extended to the field of zirconium chemistry. R. Kh. Freidlina succeeded in discovering in the field of silicon chemistry the reaction of thermal telomerization of olefins with silicoform and organic silane derivatives. This new reaction allowed the preparation of new siloxane polymers.

Studies of the chemical transformations of telomers of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes and related compounds led R. Kh. Freidlina to the establishment of the comparative chemical characterization of the reactivity of various chlorine-containing functional groups – dichloromethyl, trichloromethyl-, trichlorovinyl and others, in saturated and unsaturated compounds. R. Kh. Freidlina developed new methods of transition from compounds with various chlorine-containing functions to various types of polyfunctional organic compounds which are intermediates in the production of synthetic resins, fibers, plasticizers, lubricants and perfume substances. Her studies laid the foundation for the new field of homolytic rearrangements of aliphatic compounds in solution. In all R. Kh. Freidlina has published over 100 scientific papers including the monograph "Synthetic Methods in the Field of Chemistry of Organometallic Compounds of Arsenic."

The results of the scientific work by R. Kh. Freidlina and by the group directed by her are being introduced into industry; a new industrial process of synthesis of ω-aminoenantic and ω-aminopelargonic acids was created along with that for the by-products resulting from it. New fibers "Enant" and "Pelargon" have been prepared from these acids.

Sabir Iunusovich Iunusov – a great scientist in the field of organic chemistry, known for his studies in the chemistry of alkaloids. Under his direction there are being conducted extensive and systematic studies of the chemistry of alkaloids based on the wild flora of the Central Asiatic republics. As the result of these studies S. Iu. Iunusov and co-workers have tested some 4000 plants for alkaloid content in Central Asia and it was shown that 800 species contain alkaloids; the quantitative content of alkaloids was determined in 200 species. S. Iu. Iunusov and co-workers have isolated 150 alkaloids, among them 81 new ones. The main attention has been directed to the study of structures of the basic skeleton of the newly discovered alkaloids; structures of 28 alkaloids have been either completely or partially disclosed; these belong to the groups of aprophine, benzyltetrahydroisoquinoline, phenanthrene, indole, indophenanthridine, quinoline, acridine, pyrrolizidine and triphenylidine. S. Iu. Iunusov has studied the general reactions of aporphine alkaloids and was able to predict and prove the structures of isothebaine, talycmidine and talgemine.

S. Iu. Iunusov studied the role and the dynamics of accumulation of alkaloids in plants and gave recommendations for the more rational dates of crop collection of the technical raw materials for alkaloid production; his work on clarification of the active principles in poisonous weeds permitted the discovery of the mechanism of the ailments caused by them and allowed development of effective means of preventing these ailments.

Corresponding Member of Academy of Sciences USSR in the specialty of "Organic Chemistry and Chemistry of Labelled Atoms"

Oleg Aleksandrovich Reutov – a great organic chemist, whose main scientific studies have been devoted to the chemistry of organometallic compounds, theory of organic chemistry and chemistry of labelled atoms. A large group of his studies has been connected with the development of new methods of synthesis of organometallic compounds, the study of their properties and clarification of the ways of their practical utilization. He has suggested over 25 new methods of synthesis of organometallic compounds of mercury, arsenic, antimony, bismuth, tin and lead. On the basis of the extensive experimental material secured by him, O. A. Reutov clarified the complex problem of the mechanism of formation of organometallic compounds through the diazonium compounds; he proposed and

supported experimentally some new concepts of heterolytic mechanism of these reactions. O. A. Reutov organized an extensive study of bactericidal properties of many organometallic compounds. Among which were found some very active ones which were effective over a wide spectrum of bacteria in dilutions of millions. As the result of these studies he created the highly effective disinfectant "Diotsid" which has a practical significance and is being produced commercially.

The second direction of O. A. Reutov's work is connected with the study of the mechanism of substitution reactions at the carbon atom. The most important results have been obtained by him in the study of the mechanism of the electrophilic substitution reactions at the saturated carbon atom, this study having been made with combined use of the stereochemical and the kinetic methods. O. A. Reutov has obtained some interesting results in the study of homolytic and electrophilic reactions involving substitution at the carbon atom as studied by means of isotope exchange. These studies have fundamental interest since the regularities discovered by him in model isotope reactions may be transferred to corresponding synthetic reactions which are important in the preparation of organometallic compounds. In addition, these studies open new horizons for the clarification of structures of active complexes. O. A. Reutov has published about 100 scientific papers including his monograph "The Theoretical Problems of Organic Chemistry" (1956).

Corresponding Members of the Academy of Sciences USSR in the specialty of "Chemistry of High Polymers"

Boris Aleksandrovich Dolgoplosk – a great scientist in the field of organic chemistry and the chemistry of high polymers. The scientific work of B. A. Dolpoplosk is mainly devoted to the study of the mechanism of polymerization processes, inhibition of radical processes and synthesis of new types of synthetic rubber. The first group of his studies was connected with the work on the phenomenon of oxidation-reduction initiation of radical processes. The results of the work on the study of the activating effect of various reducing agents on the process of decomposition of diazoaminobenzene and on the polymerization process have been utilized in industry (emulsion polymerization of butadiene) and have been rewarded by the Stalin Prize.

B. A. Dolgoplosk has carried out a series of studies on the synthesis of new polymers, on the study of the connection between structure of polymers and their properties. Many studies have been adopted by the synthetic rubber plants. The systematic studies of the phenomenon of oxidation-reduction initiation have led him to the development and the study of new systems which are capable of initiating various radical processes at low temperature. B. A. Dolgoplosk's theoretical investigations, collected in the monograph "Studies in the Field of Polymerization" have been rewarded by the Stalin Prize in 1948. He carried out a series of studies of reactions of various free radicals in solution. B. A. Dolgoplosk studied the inhibition of radical reactions in the processes of thermal and initiated polymerization, hydrocarbon oxidation and decomposition of peroxides. In recent years he has widely extended his work on the study of the catalytic polymerization process. Solid thermally stable polymers of butadiene and isoprene with high softening points were synthesized on the basis of the catalytic method of polymerization.

Aleksei Andreevich Korotkov – a well-known scientist in the field of chemistry of high polymers. He took an active part in the organization of production of synthetic rubber; he developed the industrial method of oxidation of ethylene into ethylene oxide and carried out investigations on industrial synthesis of a number of products from ethylene oxide, on isolation of ethylene from waste gases of synthetic rubber industry. Under his direction there were carried out the studies on the improvement of the methods of treatment of by-products of the synthetic rubber industry (higher alcohols and hydrocarbons), on the synthesis of ethylene cyanohydrin, acrylonitrile, etc. His systematic studies of polymerization of divinyl and vinyl compounds by alkali metal catalysts have led to important theoretical results: the effect of the nature of the radical in organolithium compounds on the rate of polymerization reaction was established and the effect of complex-forming compounds on the direction of polymerization reactions of isoprene and butadiene was discovered; the dependence of the copolymerization constants on the nature of the metal in organometallic compounds and on the nature of the solvent was discovered; kinetics of polymerization of butadiene, isoprene, diisopropenyl and styrene by organometallic compounds was studied.

A. A. Korotkov created the method of polymerization of butadiene in a continuous apparatus. The resulting rubber has a high resistance to low temperatures and has more regular microstructure. A great accomplishment made by A. A. Korotkov was his synthesis of polyisoprene rubber which is close to the properties and the structure of natural rubber. He developed the technology and prepared over 100 tons of S.K.I. rubber. Recently A. A. Korotkov began a study of the mechanism of action of new catalysts based on the metal halides of variable valence and organometallic compounds.

Corresponding Member of Academy of Sciences USSR in the specialty of "Radiochemistry"

Viktor Mikhailovich Vdovenko – a great scientist-radiochemist; author of over 90 scientific publications, mainly on radiochemistry and inorganic chemistry. His first studies were devoted to the behavior of ions in complex systems. In light of the theory of ion exchange, V. M. Vdovenko also studied the absorption of ions by solid electrolytes as influenced by electrochemical properties of the latter. At the same time he carried out a series of studies on hydrochemistry, followed by studies on adsorption of radium on glass.

The basic scientific studies by V. M. Vdovenko have been done in the postwar years and have a considerable significance for the national economy. Heading a large group of scientific collaborators he widely developed the scientific direction begun by B. A. Nikitin, materially added to his theories and laid an experimental foundation under them; in addition,he introduced his work into industry. A special interest, both theoretical and practical, exists in V. M. Vdovenko's work on distribution of radioactive elements between two immiscible solvents. He studied the distribution of nitrates of uranium, neptunium, plutonium and a number of other elements between aqueous solutions and some oxygen-containing organic compounds. The results of these studies opened the possibility of application of the extraction method for isolation of uranium and plutonium from aqueous solutions and their purification from the fissional elements. The basic principles of the extraction method of treatment of irradiated uranium were worked out. V. M. Vdovenko is one of the more authoritative scientists in the field of extraction chemistry.

Corresponding Members of Academy of Sciences USSR in the specialty of "Physical Chemistry"

Veniamin Grigor'evich Levich – a great theoretical physicist, working in the field of kinetics of physicochemical processes and chemical technology. He created a new and important direction of work – physicochemical hydrodynamics. V. G. Levich created the general theory of particle transfer and energy transfer to the boundaries of phases in a moving fluid, which theory has a considerable significance in physical chemistry as a whole and particularly in the development of the quantitative theory of technological processes. V. G. Levich has made a great contribution to the kinetics of electrochemical reactions,created the theory of concentrational polarization in a moving medium, quantitative theory of polarographic maxima, and developed the theory of nonequilibrium double layer at the metal-solution boundary. He developed a wide sphere of problems related to capillary hydrodynamics which considers the effect of surface tension on motion of liquids. Recently V. G. Levich is developing a new direction of work – theory of the semiconductor-electrolyte solution boundary. V. G. Levich's monograph "Physicochemical Hydrodynamics" appeared in 1952; this work contains the generalization of a number of his studies and has received a wide distribution. The work by V. G. Levich has found application in various branches of chemistry and chemical technology.

Nikolai Markovich Emanuel' – one of the leading scientists in the field of chemical kinetics, author of over 80 published scientific papers on the problems of experimental verefication of chain theory, study of the mechanism of homogeneous catalysis and chemical induction, creation of new principles of stimulation of slow branched chain reactions and the direction of these processes. A large number of studies by N. M. Emanuel' was devoted to the work on intermediate products of oxidation. He was the first to discover the formation of intermediate products of free radical type during the slow branched chain reactions; he studied their kinetic behavior and accomplished a spectroscopic identification of these substances; he confirmed the important conclusion of the chain theory about the formation of high concentrations of active centers during a branched chain process. N. M. Emanuel' developed an original kinetic method of study of intermediate products which permitted a study of their kinetics during the course of the process.

N. M. Emanuel' discovered a new mechanism of homogeneous catalysis in oxidation reactions of hydrocarbons. He showed that homogeneous catalysis is realized through the succession of two time-separated chain reactions with different mechanisms. He proposed a new principle of gas initiation of chain oxidation reactions of organic compounds in liquid phase, according to which the initiating influence is effective only in the initial period of development of the reaction. N. M. Emanuel' has moved the general problem of transition of many gas phase oxidation processes from the regimes of high temperature gaseous oxidation to the regimes of mild low temperature oxidation in liquid phase by the use of the principle of gaseous initiation. These studies are prospectively useful for the chemical industry. In 1958 N. M. Emanuel' was awarded the Lenin Prize for his work on the chain reactions.

Corresponding Members of Academy of Sciences USSR in the specialty of "Technical Chemistry"

Andrei Nikolaevich Bashkirov – a great scientist in the field of chemistry and chemical technology. He pioneered in the synthesis of artificial liquid fuel from carbon monoxide and hydrogen, in the USSR. As a result of extended studies, A. N. Bashkirov and his co-workers developed a number of original syntheses based on carbon monoxide and hydrogen, by the use of new iron catalysts; they have developed a high-yield synthesis of hydrocarbons, synthesis of ethyl alcohol, synthesis of higher alcohols, direct synthesis of alkylamines, etc. A. N. Bashkirov's work with his co-workers in the field of the chemistry and the mechanism of synthesis based on carbon monoxide and hydrogen has a great significance. He was the first to prove the general nature of the mechanism of synthesis of hydrocarbons on cobalt and iron catalysts, to clarify the role of the reaction of conversion of carbon monoxide by water, and to establish some important laws of catalytic action of fused iron catalysts. A. N. Bashkirov's studies with the use of radioactive isotopes proved experimentally the unity of mechanism of formation of various organic compounds from carbon monoxide and hydrogen.

From 1946 A. N. Bashkirov has been working in the field of hydrocarbon oxidation. A deep study of the chemistry of this process has led him to the discovery of methods of control and realization of syntheses of higher alcohols, ketones, glycols and esters. In years ahead it is planned to put into operation a number of large plants for the production of the higher alcohols using A. N. Bashkirov's method. He also developed the method of desulfurization of liquid petroleum products and an original method of preparation of unsaturated hydrocarbons from dihalo substituted hydrocarbons. On the basis of this, there was created a new industrial method of isolation of styrene and indene from crude benzene. A. N. Bashkirov has published over 100 scientific papers.

Kirill Andreevich Bol'shakov – a great scientist in the field of chemistry and technology of rare, scattered and radioactive elements. He took part in the studies on extraction of vanadium from iron ores in Kerch Peninsula and titanomagnetites in Ural. This work was completed by the organization of vanadium production in the USSR. For the development of the technology of production of ferrovanadium K. A. Bol'shakov was awarded the Stalin Prize.

Later scientific work of K. A. Bol'shakov was devoted to the problem of isolation of cobalt from native polymetallic ores; he developed the technology of preparation of cobalt from arsenic-bearing and other ores. These studies laid the foundation for the industrial production of cobalt in USSR.

As the result of the many studies made by K. A. Bol'shakov on the problems of isolation of scattered elements from wastes and intermediates of industrial origin, there was organized the industrial preparation of pure gallium, indium, thallium and rhenium.

Much interest exists in K. A. Bol'shakov's work on the study of physicochemical basis of technological processes of preparation of rare elements and the lesser metals (process of preparation of antimony and bismuth by precipitative fusion, processes of chlorinating and sulfatizing calcination of cobalt-nickel ores and products of their treatment, conditions of precipitation of compounds of rare elements from solution, etc.).

During the recent years K. A. Bol'shakov has completed a number of important studies for which he was rewarded by a Stalin Prize.

Iusuf Geidarovich Mamedaliev – a great specialist in the field of chemistry of petroleum. His work on the reactions of alkylation of aromatic, paraffinic and cycloparaffinic hydrocarbons served as a basis for the industrial synthesis of high-quality components of aviation fuels. Iu. G. Mamedaliev was awarded the Stalin Prize for these studies. He also made some extensive studies of alkylation of benzene and its derivatives, alkylation of naphthalene, anthracene, phenanthrene and a series of cyclanes with the further transformation of the resulting alkyl-substituted hydrocarbons into the corresponding alkylarylsulfonates of various metals – new monomers and emulsifiers for the rubber industry and effective additives for improvement of quality of lubricating oils and fuels.

Studies made by Iu. G. Mamedaliev in the field of halogenation of petroleum gases has a considerable theoretical and practical significance for the petrochemical industry. A number of processes developed by Iu. G. Mamedaliev have been prepared for industrial utilization (production of carbon tetrachloride, methyl chloride, methylene bromide, etc). A large investigative scope of work was extended by him to the catalytic treatment of petroleum products, creation of methods of preparation of high-quality reactive fuels and synthetic detergents from the wastes of the petroleum industry. Iu. G. Mamedaliev has published over 100 scientific papers and a number of monographs.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

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